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Drinking Water Pilot Project Report IIA

Advanced Treatment Technology

Karlsruhe, F.R.G.

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16. ABSTRACT

This report is a compilation of the papers presented at the EPA sponsored international conference held in Karlsruhe, Federal Republic of Germany, in September 1978. It discusses the problem of controlling health hazardous organo-chloro compounds resulting from traditional chlorination of drinking water and the oxidation techniques that can potentially remedy that problem. These include 1) changing or eliminating points of chlorination in conjunction with modification of other treatment processes, 2) ozonation for different durations and conditions at different points of conventional treatment, 3) biological oxidation in slow filter media (e.g., sand, activated carbon) and within the ground (riverbank filtration) and 4) use of chlorine dioxide, ultraviolet light and hydrogen peroxide, and potassium permanganate. These other oxidants, however, may introduce other chemicals of currently unknown health risk. Removal of other contaminants (e.g., bacteria, virus, ammonia, iron, manganese, trace metals) are also discussed.

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University of Karlsruhe

OXIDATION TECHNIQUES IN DRINKING WATER TREATMENT

Papers presented at the Conference held in Karlsruhe,
Federal Republic of Germany, September 11 - 13, 1978

Compiled and edited by

Dr.-Ing. W. Kühn and
Prof. Dr. H. Sontheimer

Karlsruhe, 1979

PREFACE

This volume contains the complete manuscripts of all lectures given by numerous leading scientists and engineers from many countries at the Conference on

"OXIDATION TECHNIQUES IN DRINKING WATER TREATMENT"

held in Karlsruhe, Federal Republic of Germany, in September 1978.

This conference was the tenth event in the series of lectures on special problems of water technology, held annually in turn at Berlin, Munich and Karlsruhe. It was also a meeting of the NATO-CCMS Study (CCMS: Committee on the Challenges of Modern Society) on Modern Problems of Drinking Water Supply.

Due to the participation of so many experts from different countries, these reports present a complete survey of all modern problems in the application of oxidation techniques in drinking water treatment. They also contain the latest results of practical and basic research as well as an outlook on future developments.

The editors wish to thank

- the German Federal Ministry of the Interior for the financial support
- the lecturers, discussion-leaders and -participants for the accurate preparation of their papers and for their valuable contribution to the conference
- the members of our Institute and of the DVGW Research Department who helped in organizing the conference, and
- Mrs. Ilse Hein and Mr. Bernd Frick for their help in compiling these reports for publication.

Karlsruhe, 1979

W. Kühn   H. Sontheimer

INTRODUCTION

Many of the industrialized Nations today face problems such as population, energy, and protection of the environment. In order to optimise use of the scientific and technical expertise from different countries, the Committee on the Challenges of Modern Society (CCMS) was created between the Allied nations of the North Atlantic Treaty Organization. This international society of scientists strengthens ties among members of the North Atlantic Alliance and permits NATO to fill a broader social role with non-member countries. CCMS has been responding to the increasingly complex, technological problems facing modern society.

A particular problem concerning many Nations is organic chemical contamination in finished drinking water supplies. This contamination results from industrial and municipal discharges, urban and agricultural run-off, degradation of naturally occurring organic material, and probably primarily in many cases from the reaction of disinfectants such as chlorine ozone or chlorine dioxide with these substances during the treatment process. Some of these chemicals, even in the low concentrations found in drinking water, may be a human health risk. In order to address this problem and benefit from international collaboration, the United States Environmental Protection Agency initiated the Drinking Water Pilot Project. The pilot study is evaluating the problems and their solutions in the following six areas of drinking water supply science and technology:

I. Analytical Chemistry
II. Advanced Treatment Technology
III. Microbiology
IV. Toxicology
V. Reuse of Water Resources
VI. Ground Water Protection

Two major components of the NATO-CCMS Drinking Water Pilot Project were two international conferences entitled Oxidation Techniques in Drinking Water Treatment and Practical Application of Adsorption Techniques in Drinking Water. These Conferences were held in Karlsruhe, Federal Republic of Germany, between September 9-13, 1978, and in Reston, Virginia, on April 30, May 1 and 2, 1979, respectively. The Reston conference, sponsored by EPA, included presentations on the toxicology of organic chemicals, the analytical chemistry of monitoring for organics, and advanced adsorption treatment technology. The Karlsruhe conference was the tenth of a series on the special problems of water technology held annually in turn at Berlin, Munich, and Karlsruhe. This conference was supported by the Federal Republic of

Germany and was arranged by the DVGW Research Department at the Engler-Bunte Institute of the University of Karlsruhe, FRG. Experts from more than ten countries presented papers giving a survey of oxidation processes, reports on recent results of research, and operational experience gained at water treatment plants.

Treatment of surface waters for use as drinking water should include flocculation, sedimentation, filtration, and disinfection in order to ensure microbiological quality and low turbidity. These two conferences, however, were concerned primarily with treatment steps that could remove organic chemicals. Speakers at the Karlsruhe conference discussed five different methods of organics removal by the use of oxidation techniques. First, tests with different waters have shown that preozonation can improve flocculation efficiency. Secondly, as a result of biological oxidation, pretreatment of water by the use of storage basins can increase the removal efficiency of suspended solids. Third, the formation of halogenated organic compounds can be avoided if chlorine dosages are controlled so that there is no free chlorine residual. Next, riverbank filtration can result in a 50-75 percent reduction of dissolved organic carbon (DOC). Finally, the advantages of increased biological oxidation in sand or carbon filters by treating water before filtration with ozone was also discussed.

This first of two reports from the Drinking Water Pilot Project, Group II, Advanced Treatment Technology, is a tribute to the efforts of Professor Dr. Heinrich Sontheimer and Dr. Wolfgang Kühn, who conceived and produced it, the FRG that sponsored it, and to the spirit of international cooperation for mutual benefit that has been a keynote of the entire Pilot Project. We look forward to continuing the ties that have developed as a result, and to the remaining reports of this series developed by the Drinking Water Pilot Project participants.

Joseph A. Cotruvo
U.S. Environmental Protection Agency
Project Chairman
Washington, D.C., USA
1979

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AUTHORS

H. Bader	Eidg. Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz (EAWAG), CH-8600 Dübendorf, Switzerland
Dr. L. Berglind	Norwegian Institute for Water Research, Postbox 333, Blindern, Oslo 3, Norway
Prof. Dr. H. Bernhardt	Wahnbachtalsperrenverband, Postfach 27, D-5200 Siegburg 1, F.R.G.
Dr. A. Bousoulengas	Scientific Research and Technology Agency, Vassileos Constantinou 48, Athens 501, Greece
J. Chedal	Compagnie Génèrale des Eaux, Siège Social, 52 rue d'Anjou, F-75384 Paris Cedex 08, France
Dr. L. Coin	Ministère de la Santé et de la Direction Génèrale de la Santé, 20 rue d'Estrées, F-75007 Paris, France
Dr. J.A. Cotruvo	Office of Drinking Water, United States Environmental Protection Agency, 401 M. Street, S.W., Waterside Mall, WH 550, Washington, D.C. 20460, U.S.A.
Dr. T.A. Dick	Department of the Environment, 2 Marsham Street, London, S.W.1, England
K. Eimhjellen	SINTEF-Dept. of Chemical Technology, University of Trondheim-NTH, N-7034 Trondheim, Norway
Dr. E. Gilbert	Institut für Radiochemie, Kernforschungszentrum Karlsruhe, Postfach 3640, D-7500 Karlsruhe 1, F.R.G.
Dr. E. Gjessing	Norwegian Institute for Water Research, Postbox 333, Blindern, Oslo 3, Norway

Dr. C. Gomella	S.E.T.U.D.E., 27 Boulevard des Italiens, F-75002 Paris, France
Dr. J.B. Goodall	Medmenham Laboratory, Water Research Centre, P.O.Box 16, Medmenham, Marlow, Bucks. SL7 2HD, England
Dr. E. de Greef	National Institute for Water Supply, Chemical Biological Division, P.O. Box 150, AD 2260 Leidschendam, The Netherlands
G. Halmø	SINTEF-Dept. of Chemical Technology, University of Trondheim-NTH, N-7034 Trondheim, Norway
Dr. T. Hedberg	Department of Water Supply and Sewerage, Chalmers Tekniska Högskola, Sven Hultins Gata 8, Göteborg, Sweden
Dr. E. Heinonen	Helsinki City Waterworks, Pasilankatu 41, SF-00240 Helsinki, Finland
A.G. Hill	Department of Chemical Engineering, College of Engineering, Louisiana University, Ruston, Louis. 71270, U.S.A.
Dr. J. Hoignê	Eidg. Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz (EAWAG), CH-8600 Dübendorf, Switzerland
Dr. O. Hoyer	Wahnbachtalsperrenverband, Postfach 27, D-5200 Siegburg 1, F.R.G.
Dr. J. Hrubec	National Institute for Water Supply, Chemical Biological Division, P.O.Box 150, AD 2260 Leidschendam, The Netherlands
Dr. M. Jekel	Engler-Bunte-Institut, Bereich Wasserchemie, Universität Karlsruhe, Postfach 6380, D-7500 Karlsruhe 1, F.R.G.
Dr. B. Josefsson	Department of Analytical Chemistry, University of Gothenburg, S-40220 Gothenburg, Sweden

Dr. V.J. Kimm	Office of Drinking Water, United States Environmental Protection Agency, 401 M. Street, S.W., Waterside Mall, WH 550, Washington, D.C. 20460, U.S.A.
Dr. N. Kirmaier	Institut für Biomedizinische Technik, Museumstr. 1, D-8000 München 22, F.R.G.
M. Klotz	Institut für Hygiene und Mikrobiologie, Universität des Saarlandes, Bau 43, D-6650 Homburg/Saar, F.R.G.
Dr. K. Kötter	Gelsenwasser AG, Postfach 769, D-4650 Gelsenkirchen, F.R.G.
Dr. D. van der Kooij	The Netherlands Waterworks, Testing and Research Institute - KIWA Ltd., Rijswijk, The Netherlands
Prof. Y. Kott	Environmental and Water Resources Engineering, Technion-Israel Institute of Technology, Technion City, Haifa 32000, Israel
Dr. J.C. Kruithof	KIWA N.V., Wiers 17, Nieuwegein, The Netherlands
Dr. W. Kühn	Engler-Bunte-Institut, Bereich Wasserchemie, Universität Karlsruhe, Postfach 6380, D-7500 Karlsruhe 1, F.R.G.
Dr. H. Kußmaul	Institut für Wasser-, Boden- und Lufthygiene des Bundesgesundheitsamtes, Aussenstelle Frankfurt/Main, Kennedyallee 97, D-6000 Frankfurt 70, F.R.G.
H. Lamblin	Compagnie Générale des Eaux, Siège Social, 52 rue d'Anjou, F-75384 Paris Cedex 08, France
Dr. J.P. Legeron	Trailigaz, 29-31 Bd de la Muette, F-95140 Garges les Gonesse, France
H. Lienhard	Engler-Bunte-Institut, Bereich Wasserchemie, Universität Karlsruhe, Postfach 6380, D-7500 Karlsruhe 1, F.R.G.

Dr. B. Lindgren	Swedish Forest Products Research Laboratory, Box 5604, S-11486 Stockholm, Sweden
Dr. D. Maier	Zweckverband Bodenseewasserversorgung, D-7770 Überlingen-Süßenmühle, F.R.G.
J. Mallevialle	Société Lyonnaise des Eaux et de l'Eclairage, 10 rue de la Liberté, F-78230 Le Pecq, France
Dr. W.J. Masschelein	Laboratoires C.I.B.E., 764 Chaussée de Waterloo, B-1180 Bruxelles, Belgium
Dr. A.P. Meijers	KIWA N.V., Wiers 17, Nieuwegein, The Netherlands
G.W. Miller	Public Technology, Inc., 1140 Connecticut Avenue, NW, Washington, D.C. 20036, U.S.A.
C.F. Morra	Chemical Biological Division, National Institute for Water Supply, P.O.Box 150, AD 2260 Leidschendam, The Netherlands
Prof. J.C. Morris	Division of Applied Sciences, Harvard University, 127 Pierce Hall, Cambridge, Mass. 02138, U.S.A.
Prof. Dr. Gertrud Müller	Institut für Wasser-, Boden- und Lufthygiene des Bundesgesundheitsamtes, Corrensplatz 1, D-1000 Berlin 33, F.R.G.
Dr. J.A. Myhrstad	National Institute of Public Health, Geitmyrsveien 75, Oslow 1, Norway
T. Nemeth	Gothenburg Water- and Sewage-Works, Fack, S-40110 Gothenburg, Sweden
Sabine Normann	Stadtwerke Wiesbaden AG, Kirchgasse 2, D-6200 Wiesbaden, F.R.G.
Dr. H. Overath	Stadtwerke Wiesbaden AG, Kirchgasse 2, D-6200 Wiesbaden, F.R.G.
Dr. G.J. Piet	Chemical Biological Division, National Institute for Water Supply, P.O.Box 150, AD 2260 Leidschendam, The Netherlands

Prof. Dr. K.-E. Quentin	Institut für Wasserchemie und Chemische Balneologie, Technische Universität München, Marchionistr. 17, D-8000 München 70, F.R.G.
Dr. R.G. Rice	Jacobs Engineering Group, 1511 K Street, N.W., Suite 835, Washington, D.C. 20005, U.S.A.
Dr. Y. Richard	Degrémont Traitement des Eaux, P.B. 46, F-92151 Suresnes, France
Prof. P.V. Roberts	Environmental Engineering, Department of Civil Engineering, Stanford University, Stanford, California 94305, U.S.A.
Dr. C.M. Robson	Department of Public Works, 2460 City-County Building, Indianapolis, Indiana 46204, U.S.A.
Dr. J.J. Rook	Drinkwaterleiding Rotterdam, Postbus 1166, Rotterdam, The Netherlands
C. Roos	Department of Analytical Chemistry, University of Gothenburg, S-40220 Gothenburg, Sweden
R. Sander	Engler-Bunte-Institut, Bereich Wasserchemie, Universität Karlsruhe, Postfach 6380, D-7500 Karlsruhe 1, F.R.G.
Dr. K. Schmidt	Institut für Wasserforschung GmbH Dortmund, Deggingstr. 40, D-4600 Dortmund 1, F.R.G.
P. Schulhof	Compagnie Génerale des Eaux, Siège Social, 52 rue d'Anjou, F-75384 Paris Cedex 08, France
Prof. Dr. R. Schweisfurth	Institut für Hygiene und Mikrobiologie, Universität des Saarlandes, Bau 43, D-6650 Homburg/Saar, F.R.G.
Dr. E. Skipperud Johansen	National Institute for Public Health, Geitmyrsveien 75, Oslo 1, Norway
Prof. Dr. H. Sontheimer	Engler-Bunte-Institut, Lehrstuhl und Bereich für Wasserchemie, Universität Karlsruhe, Postf. 6380, D-7500 Karlsruhe 1, F.R.G.

Dr. T. Stenström	Department of Environmental Hygiene, The National Swedish Environment Protection Board, Fack, S-10401 Stockholm, Sweden
Dr. A.A. Stevens	Drinking Water Research Division, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268, U.S.A.
Dr. J.M. Symons	Water Supply Research Division, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268, U.S.A.
Dr. T. Thorsen	SINTEF-Dept. of Chemical Technology, University of Trondheim-NTH, N-7034 Trondheim, Norway
Dr. P. Toft	Environmental Health Centre, Tunney's Pasture, Ottawa, Ontario K1A OL2, Canada
Dr. G. Uhlig	Stadtwerke Duisburg AG, Postf. 100246, D-4100 Duisburg 1, F.R.G.
J. Valenta	Wasserversorgung Zürich, Hardhof 9, CH-8023 Zürich, Switzerland
Dr. D. Weil	Institut für Wasserchemie und Chemische Balneologie, Technische Universität München, Marchionistr. 17, D-8000 München 70, F.R.G.
P. Werner	Institut für Hygiene und Mikro- biologie, Universität des Saarlandes, Bau 43, D-6650 Homburg/Saar, F.R.G.

DEVELOPMENT, PROBLEMS, AIMS, AND SIGNIFICANCE OF THE OXIDATION PROCESS IN THE TREATMENT OF DRINKING WATER

H. Sontheimer

Introduction

Ever since it was found, first in the Netherlands and somewhat later in the USA (1,2), that in the chlorination of water - a disinfection and oxidation process used both then and now in nearly all waterworks - chloroform and other haloform compounds can be formed in large quantities, increasing attention has been paid both in practice and research to the oxidation processes in the treatment of drinking water. This trend became even more marked after studies on the total amount of organically bound chlorine, particularly those in Karlsruhe, had shown that as a rule the amount of this is greater by a factor of 5 - 10 than the amount of haloforms or chloroform (3). A typical result of such work is illustrated in Fig. 1.

The figure shows the results from the chlorination of pure humic acid solutions of various concentrations with the same amount of chlorine (20 mg/l) after a reaction time of almost 24 h.

It can be seen that only about one-sixtieth of the chlorine added has been converted into chloroform, while the greater part of it is bound in polar compounds which can be gas-chromatographed only with difficulty. Some of the latter compounds were only formed by the likewise very considerable purely oxidative action of chlorine.

From these and many other results, more detailed reports on which are given in other lectures, it has become evident that even a process like chlorination, which has important

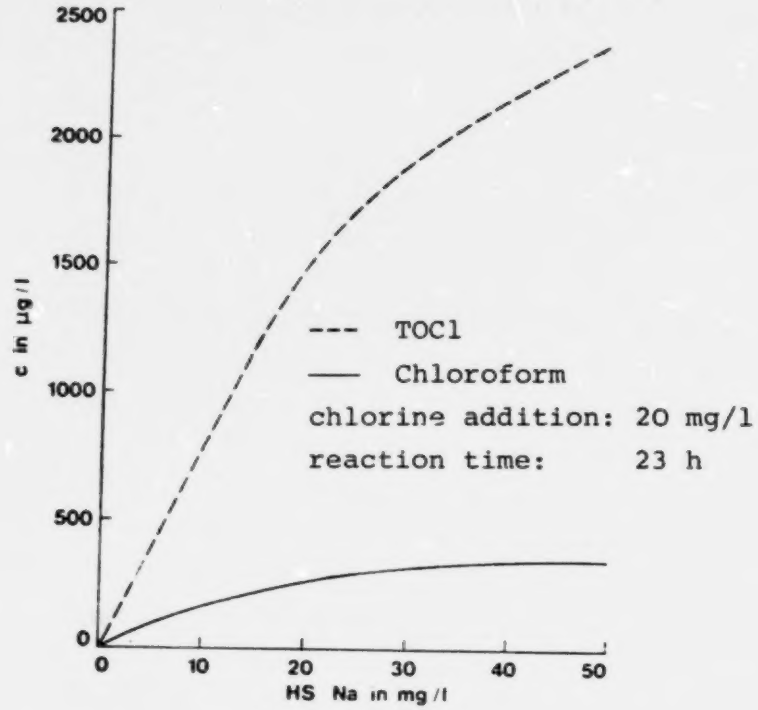


Fig. 1 Dependence of chloroform and TOCl on the concentration of humic acid

advantages for water treatment, can have clear limitations as regards its applicability, and that it is impossible to solve all problems of water quality just by adding more chlorine.

As with chlorination and its beneficial and adverse effects, we are concerned today, induced by the developments just discussed, with other similar treatment processes and with the aims of drinking-water treatment in general.

An attempt to summarize briefly the experience and consequences that have emerged in the last few years can in my view be reduced to the following points:

TABLE 1 BASIC PRINCIPLES ON DRINKING-WATER TREATMENT

The aim of all measures in drinking-water treatment is to obtain a

"naturally pure drinking water"

An optimum drinking-water treatment requires the use of suitable processes in a sensible combination, with observation of the following requirements:

- Reliable and extensive removal of all harmful substances
- Avoidance of new formation or enrichment of harmful substances
- Adaptability to changed properties of raw water

Processes for drinking-water treatment may also have undesired effects on the quality of drinking water

1) The aim of all measures in the treatment of drinking water is to obtain a "naturally pure drinking water".

2) An optimal treatment of drinking water requires the use of suitable processes in a sensible combination, with observation of the following demands:

   a) reliable and far-reaching removal of all anthropogenic and naturally formed perturbing materials,

   b) avoidance of new formation or enrichment of perturbing materials in the course of the treatment itself,

c) reliable effectiveness even when the properties of the raw water are changed,

d) simple and effective control of the operation.

3) The processes used for treating drinking water can also have undesirable effects on the water quality if they are mis-applied.

In this admittedly incomplete list the last point has gained particular significance in recent years on the basis of the experience with chlorination, and has certainly contributed to the fact that the aims of the treatment of drinking water, i.e. the quality requirements for a given drinking water, are an object of increasing consideration. Although we cannot go into closer details of this problem within the framework of this lecture, it seems necessary to make some further statements on this question and on the first point in the above list.

"Naturally pure" or only "safe" drinking water

In all countries there are laws and decrees ensuring the supply of "safe" drinking water, i.e. ensuring that the use and consumption of drinking water has no undesirable effects on health. To illustrate this point, we may quote the Safe Drinking Water Act in the United States (4), or the Drinking Water Act of the German Federal Republic (5). In general, regulations of this kind lay down limiting values for a series of different parameters, which must be complied with in the drinking water.

What we must ask, however, is whether a drinking water is really safe when the threshold values are strictly adhered to. Do we have a sufficiently reliable and safe basis for laying down the limiting values and do we possess the necessary methods of foolproof control, especially when a large nunber of individual limiting values has been fixed? The answers to these questions are relatively easy and affirmative in the case of the undesirable inorganic materials, e.g. heavy metals, but it is almost impossible to specify any limiting values when we turn to the wide range of unwanted organics. The number of individual substances so far detected analytically in drinking waters now comprises almost 1000 separate compounds, and as our analytical expertise increases new compounds are found practically every day and their behaviour is checked with various treatment procedures. Although they are important and useful in individual cases, limiting values alone are not enough. We neither know exactly which individual organic compounds are present in a particular water, nor can we establish by simple methods what toxicological effects these substances may exert, especially when it comes to cumulative effects.

On the other hand, we do need rules for the treatment of water, we need information on the treatment plant required for each raw water, on the purification effects that must be achieved, and on how the efficacy of these can be established independently of the variations in the raw water quality. From this point of view it is understandable that attempts are made from time to time to lay down rules on the selection of treatment processes. In the formulation of the laws and decrees it must be borne in mind, as already mentioned earlier, that the processes used for the drinking-water treatment can have not only beneficial but also undesirable effects on the quality of the drinking water. The following summary shows the cause of the difficulties on some especially important examples. (Table 2)

TABLE 2 UNDESIRABLE EFFECTS OF IMPERFECT USE OF PROCESSES FOR DRINKING-WATER TREATMENT

Process used	Possible undesirable effects of process if:	
	Efficiency too low	Treatment too extensive
Chlorination	insufficient disinfection	formation of organochloro compounds
Removal of organics by adsorption	residual amount of harmful substances is too high	increased tendency to corrosion
Flocculation	insufficient removal of colloids	high concentration of neutral salts
Oxidation with ozone	insufficient effect	germ formation in network
Softening	interference by precipitation of $CaCO_3$	increased tendency to corrosion increased tendency to myocardial infarction

The table indicates above all that the correct dosage, e.g. in oxidation processes, is of great significance if the final aim is not only the achievement of the process advantages but also the avoidance of its disadvantages.

The conclusions emerging from the summary are only examples. In reality the situation is considerably more complicated, as can be seen from Table 3.

TABLE 3 GRANULAR ACTIVATED CARBON FILTERS

ADVANTAGES	DISADVANTAGES
Specific removal of dangerous organics	Not very effective for THM removal
Good efficiency at peak concentrations	Chromatographic effects after longer running times
High loadings at the top layer	Long working zone and partial breakthrough of organics
Partial regeneration through biological degradation of adsorbed organics	High bacteria counts in the effluent
Additional filtration and turbidity removal	Backwashing problems, small carbon particles in the effluent
Easy handling and operation	Difficult breakthrough control

In this table both the many advantages and the disadvantages of activated carbon filtration have been compiled for a report in the USA. Here it was intended to prescribe the details of the use of activated carbon filters for the treatment of chemically polluted river waters, together with the basic dimensioning and mode of operation.

While the details of this table will not be discussed further here, it can be seen that the correct layout and operation of a filtration plant of this kind are determined by a whole series of quantities and their relationships. Only if these are suitably taken into account will the use of activated carbon filters be truly advantageous for the water quality. These aspects, here only briefly outlined, are very difficult to incorporate in a single law. Moreover, it is not merely a question of the raw water quality but also of the process scheme of the treatment plant. This applies especially to oxidation processes.

Before going into greater detail another proposal should be discussed, which is of particular significance for an evaluation of drinking-water quality and which is formulated particularly clearly in the German DIN 2000 standard (6).

TABLE 4 GENERAL CRITERIA FOR DRINKING WATER QUALITY

DIN 2000 (Germany)

Drinking water quality should be similar to a -

water from the natural cycle,
without anthropogenic impurities,
taken from safe depth,
after a long retention time,
as an oxygen-containing ground water.

According to this, all measurable parameters of drinking-water quality should be oriented at the properties of a water extracted from the natural water cycle as oxygen-containing ground water without any anthropogenic constituents and which can be used directly as high-quality drinking water without additional treatment, i.e. without additional chlorination.

This type of positive characterization and orientation at a "naturally pure" drinking water enables us to draw specific conclusions about the optimal kind of treatment in each individual case. This is because, even today, there are still a number of ground water sources with favourable properties of this kind. In addition, we know the connections, processes, and natural laws that determine the composition of natural water of this kind, and anthropogenic influences can be analysed well by measuring group parameters.

Viewed in this way, the evaluation of the water quality provides appropriate criteria for the evaluation and the adoption of oxidation processes.

Aims and effects of oxidation processes

From the commencement of centralized drinking-water supply the oxidation processes have been among the most important treatment steps, since - if performed correctly - they guarantee reliable disinfection and so contribute decisively to safety of the water. It is therefore no surprise that this aim has very often been in the foreground of interest in the evaluation of various oxidizing agents and oxidation processes, as is still the case today. Within the framework of this conference, too, many reports were concerned with the problems connected with oxidation.

However, the great significance of the disinfecting action of oxidation processes should not obscure the fact that disinfection is only one of the aims in which success can be achieved with these processes.

TABLE 5 OBJECTIVES OF OXIDATION PROCESSES

1) Disinfection

2) Removal of organic constituents of water

   A) Complete oxidation:

$$4C_nH_mO_q + (4n + m - 2q)\ O_2 = 4n\ CO_2 + 2m\ H_2O$$

   B) Partial oxidation with subsequent more comprehensive purification

3) Transformation of organic constituents of water e.g. improvement of corrosion behaviour

4) Oxidation of inorganic undesirable materials e.g. Fe, Mn, NH_4^+

5) Combination of objectives 1 - 4

As can be seen from the table, oxidation processes play an important part both in the removal and in the transformation of undesirable organic and inorganic constituents of the water, and are now used successfully in many waterworks to achieve these objectives.

In those cases where the complete removal of unoxidized substances is achieved in a subsequent process, it is of no importance concerning the final quality of the final water whether the oxidation taking place is complete, to CO_2 and H_2O - as is generally the case in biological oxidation processes and with biologically degradable substances - or whether the oxidation is only partial - such as is the case with chemical oxidation, especially with the use of ozone. Many such combined processes are known today. On account of their major importance, they will be discussed in more detail later in connection with the placing of oxidation processes within the overall sector of drinking-water treatment.

At this point it seems appropriate to consider in greater detail an aspect to which insufficient attention is often paid in the performance and evaluation of oxidation processes. This is the transformation of organic water constituents by oxidation, mentioned under point 3 in Table 5. In the practice of drinking water treatment two important effects are at work here.

In the first place, the molecular-weight distribution of the organic water constituents is modified by oxidation treatment, here discussed on the example of ozone. The following figure shows some results of such studies on the basis of experiments with biologically purified domestic waste water.

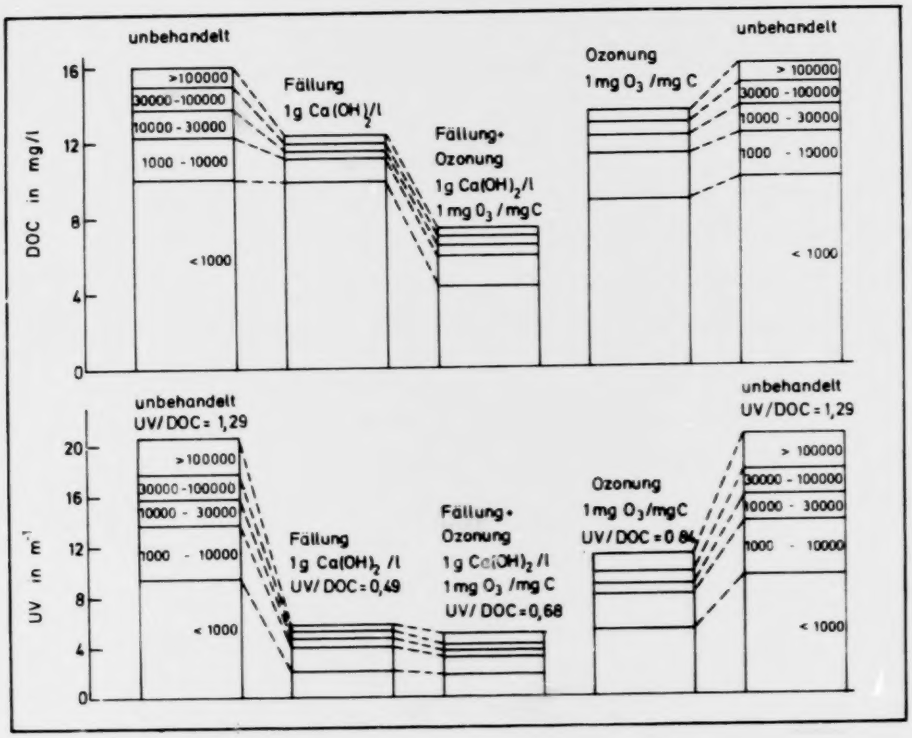


Fig. 2 Change of DOC- and UV-values upon ozonation and precipitation in biologically pretreated waste-water (Berghausen)

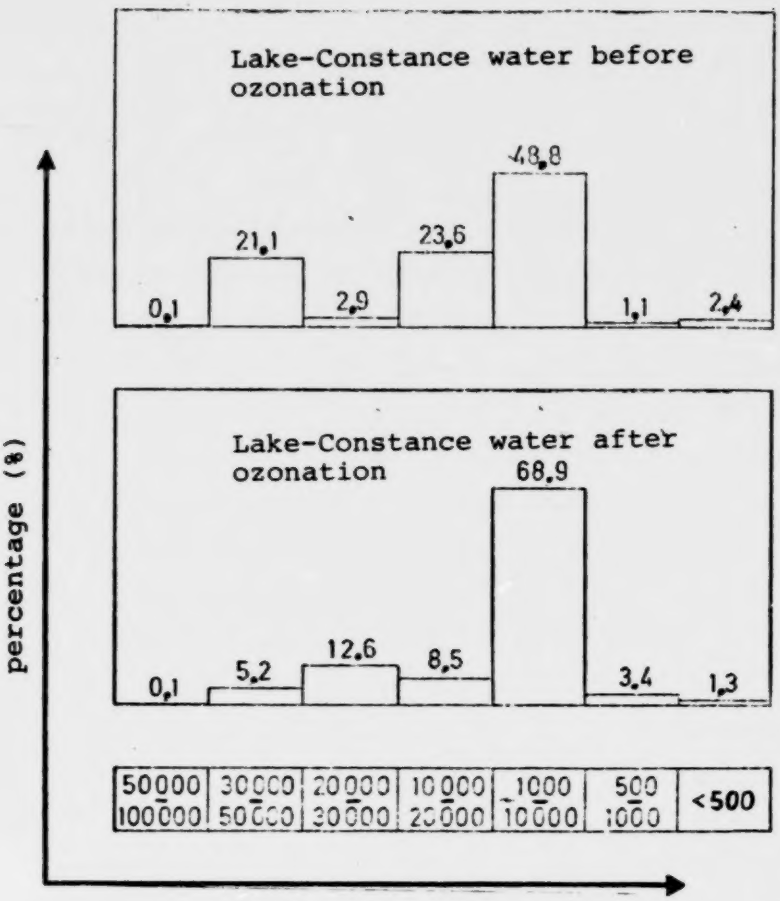
unbehandelt = untreated; Fällung = precipitation;

Fällung + Ozonung = precipitation + ozonation

The figure gives results obtained within the framework of a project sponsored by the Federal Department for Research and Technology on the optimization of the use of ozone, the DOC and UV values, divided into molecular-weight fractions. From the values given at the extreme right and left of the figure for the raw water it can be seen that the greater part of the organic material in this purified waste water has a molecular weight of under 1000. Of course, the substances of higher molecular weight have a higher specific UV extinction. For this reason, as the lower part of the figure shows, they account for the greater proportion of the measured UV values. Since it is precisely the materials with good UV absorption and high molecular weight that are also very readily precipitated in the form of insoluble calcium salts, precipitation causes a strong reduction of the UV extinction, while the effect of precipitation on the concentration of organically bound carbon is much weaker.

The ozone treatment, in which comparatively large quantities of ozone were used here, in effect diminishes only the concentration of the lower-molecular substances. It is manifested only slightly in the UV extinction after precipitation. The situation with the direct action of ozone, represented on the right-hand side, is quite different. In this case the decrease of the DOC is much smaller than after pretreatment by precipitation, while the UV extinction undergoes a greater reduction. This effect can only be explained if it is assumed that in direct oxidation apart from the partial oxidation to CO_2 and H_2O, transformation of the organic water constituents is the main process.

The relationships in the ozonization of raw water in drinking-water treatment are very similar. Here too we can observe, as the following figure shows on the example of water from Lake Constance,



molecular-weight fraction

Fig. 3 Influence of ozone on molecular-weight distribution of humic acid from Lake Constance

a certain reduction of the molecular weight. The smaller proportions of the higher-molecular fractions and the shift towards somewhat lower molecular substances are particularly evident. The molecular-weight fraction between 1000 and 10 000 increases particularly clearly, while the low-molecular materials below 1000 undergo only a slight increase

The practical effect of this type of shift in the molecular weight is that only a small increase of the biologically readily degradable substances as a result of ozonization treatment can be established, since only a few low-molecular materials are newly formed. On the other hand, a clear enhancement of the adsorption of these substances on polar surfaces is brought about by the change in the structure - here too linked to the oxidation process - and in this case especially by a change in the polarity of the organic water constituents. This is shown in the following figure on the example of calcium carbonate.

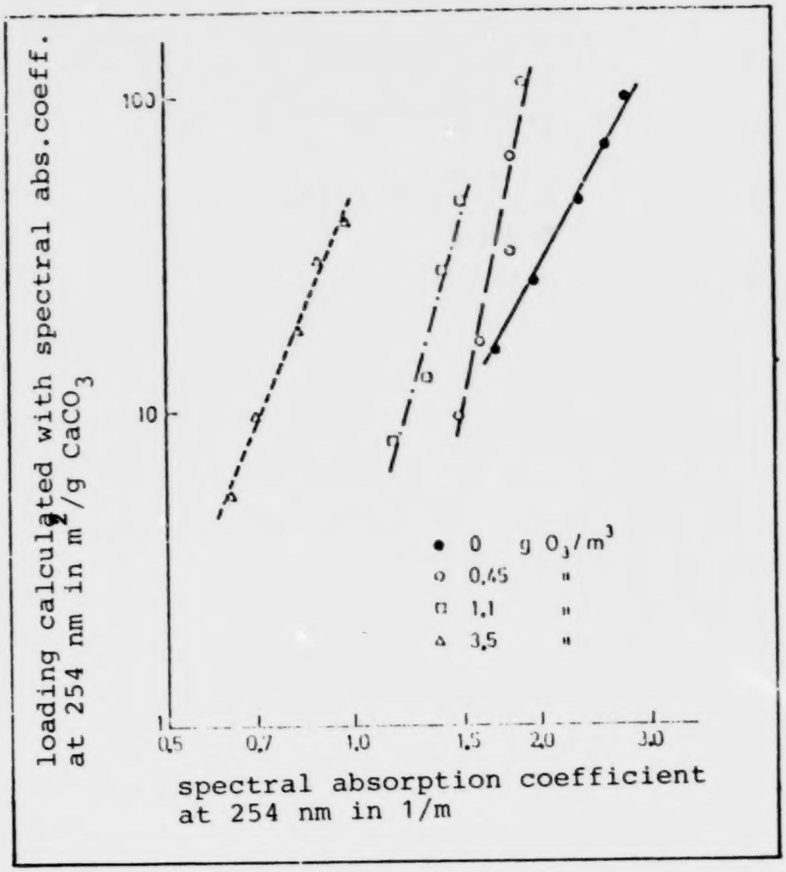


Fig. 4 Adsorption isotherms (Freundlich) of substances in Lake Constance water on calcium carbonate after different dosages of ozone

Fig. 4 presents isotherms plotted for the UV-absorbing substances in Lake Constance water. The isotherms are clearly shifted to the left as the addition of ozone is increased, i.e. in the direction of better adsorption. The same cannot be said for the non-polar activated carbon surface, where sometimes exactly the opposite effect is observed. However, it is true for polar surfaces such as are found in the case of $CaCO_3$ or of iron oxides.

The fact that this enhancement of adsorption as a result of oxidation procedures is not only of academic interest but also of practical significance is demonstrated by the following considerations and experimental results from the Karlsruhe Institute.

TABLE 6 INFLUENCE OF HUMIC ACID ON THE PRECIPITATION OF $CaCO_3$

Humic Acid	D O C in mg/l	K	Main components of molecular-weight distrib.	Acid Number
Lake Constance	0.5	0.24	20.000 - 50.000	8.0
Zurich	0.5	0.32	30.000 - 50.000 1.000 - 10.000	7.4
Haltern	1.0	0.53	500 - 10.000	8.0
Schwäb.-Hall	2.5	0.67	500 - 10.000	5.5
Hann.-Fuhrberg	4.0	0.71	500 - 10.000	4.6
Without Humic Acid	0	0.90	$- \frac{d\lvert Ca^{2+}\rvert}{dt} = K\cdot O(\lvert Ca^{2+}\rvert \cdot \lvert CO_3^{2-}\rvert - \frac{L}{f_1})$	

Among other things, the change in the precipitation rate of $CaCO_3$ was studied for humic acids from various raw waters of practical interest(7).After the addition of powdered limestone the pH was artificially increased with a solution of caustic soda. $CaCO_3$ was precipitated from the now supersaturated solution, the precipitation rate being dependent on the $CaCO_3$ supersaturation as shown in the formula in the lower right of the table. The smaller the constant K, which can be determined experimentally, the more does the humic acid hinder the precipitation of $CaCO_3$. From the numerical values of K it can be seen that the humic acids of Lake Constance and Lake Zürich are most effective. However, they have the highest mean molecular weight and as a rule higher-molecular substances are also better adsorbed.

There are also other differences between the other three humic acids, in spite of their approximately equal mean molecular weight. The acid numbers are different here. The higher the acid number, the lower is the polarity of the organic material, and the better is it adsorbed. However, the extent of the adsorption determines the inhibition of the $CaCO_3$ precipitation rate and hence also the magnitude of K.

On the one hand oxidation with ozone increases the polarity of the organic material, thereby improving its adsorbability, but on the other hand it reduces the molecular weight and this leads to a deterioration of the adsorbability and so to a smaller inhibition of the $CaCO_3$ precipitation rate.

Nevertheless, with the ozone doses normally used in the treatment of drinking water, the beneficial effects predominate in most cases, as the results of the following table show on one example.

TABLE 7 K-values of $CaCO_3$-precipitation and action numbers WZ_{HS} as a function of O_3 concentration in water from the river Danube (WZ_{HS} = action number humic acid)

Treatment step of raw water of river Danube	D O C mg/l	K in $\frac{1}{\text{mol.min.mg.}}$	$WZ_{HS} = \frac{\frac{Ko}{K} - 1}{DOC}$
Flocculation	2.75	0.37	0.4
Ozonation (2.5 mg/O_3) + flocculation	2.32	0.20	1.3
Ozonation (5.7 mg/l O_3) + flocculation	1.91	0.23	1.3
Flocculation and C-removal by activated carbon (F 400)	0.20	0.80	0.0

Here the K-values were obtained after flocculation and after the addition of two different amounts of ozone, the DOC also having been reduced by this treatment. The K-values were compared with those of a water from which the organic material had been removed almost completely by flocculation and adsorption.

Both from the K-values themselves and from the action number referred to the DOC it can be seen that after the ozone treatment the organic material remaining after flocculation assumes considerably more favourable properties as regards its action on the inhibition of the $CaCO_3$ precipitation rate. Increasing ozone additions cause no further improvement. It may be deduced from this that the values of the action number will decrease again when the amount of ozone is increased further.

For the practical significance of these results it is important that completely analogous effects can be measured for the oxidation kinetics of bivalent iron and that this result can also be extended to the corrosion behaviour of steel pipes. Although it is impossible to go into details at this point, a result from field trials with Lake Constance water can be shown here, from which this connection may be discerned.

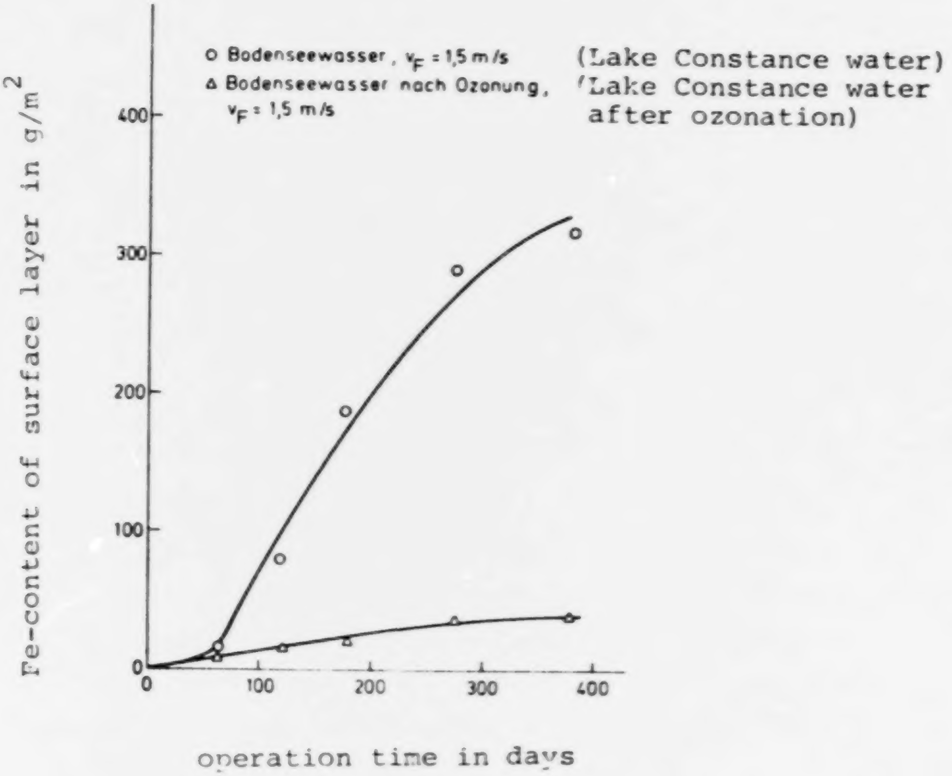


Fig. 5 Iron content of surface layer in Lake Constance water before and after ozonation

The figure gives the amount of iron in the corrosion products of a steel pipe at a flow rate of 1.5 m/sec for the almost solids-free Lake Constance water before and after ozonization and filtration. Since the amount of the corrosion products constitutes a measure of the corrosion rate, these results reveal that after ozonization a transformation had taken place in the organic material dissolved in the water of Lake Constance, such that the corrosion rate under the given conditions fell to a fraction of the corrosion rate with the raw water.

If the significance of the possible beneficial transformation of the water constituents by oxidation is to be clearly and appropriately demonstrated,the results obtained in these tests, close to actual practice, are most suitable. However, when it is considered that this effect is in no way bound to occur in a water with differently combined constituents, and that the opposite effect can occur even with the water of Lake Constance if the amount of ozone is too high, it becomes evident how difficult it can be to asses in particular test results of oxidation processes. Care is therefore needed when making general statements on the use of such procedures in drinking-water treatment. This is why so many authors and reporters are to be found at this conference, for it is only when the problems are viewed from various sides that it becomes possible to deal with them fairly completely. For this reason the rest of this paper can only be regarded as an introduction to the problems in question, with particular emphasis on some aspects that to me seem of special importance.

Survey of oxidation processes

The difficulties in obtaining a reliable and generally valid survey of the advantages, disadvantages, and the significance of individual oxidation processes in the treatment of drinking water are not only due to the fact that with these processes we are attempting to achieve a wide and varied range of aims but also to the variety of possible processes, a summary of which is provided in the following table.

TABLE 8 OXIDATION PROCESSES USED FOR THE TREATMENT OF DRINKING WATER

CHEMICAL OXIDATION with	
	Chlorine
	Chlorine dioxide
	Ozone
	Permanganate
PHYSICO-CHEMICAL OXIDATION with	
	UV irradiation
	γ-radiation
BIOLOGICAL OXIDATION with	
	Slow filtration
	Soil passage
	Biologically working filters

Accordingly, oxidation processes can be carried out in such a way that the oxidizing agent is added to the water, chlorine and ozone being used most often. The physico-chemical processes are of much smaller importance, only UV irradiation being used in a few rare cases in the practice of drinking-water treatment.

In contrast to this, biological oxidation is the mostly used oxidation process in Central Europe. The technologies used here, listed in the table, are some of the oldest methods in the treatment of drinking water.

In the course of the conference more detailed information will be given on the individual processes, so that in this introductory paper only some especially important aspects of three of them will be considered, namely chlorination, ozonization, and biological oxidation.

In connection with the various objectives of oxidation processes already mentioned, it must first be said that nearly all these processes can be used both for the oxidation of organic and inorganic water constituents and for disinfection. The two aims are often combined. However, in recent years experience has shown that it is particularly useful to separate these aims by the combined use of different oxidation methods. Moreover, rather than using two oxidation processes simultaneously, e.g. ozone and UV irradiation, it is preferable to apply two processes in succession. The best known and by far the most important example of this is the combination of chemical and biological oxidation, the particular aim of which is to convert biologically resistant materials into degradable ones by chemical oxidation and so to achieve a more extensive and efficient biological oxidation (8). The importance of this procedure was first realized after it had become known that by means of high chlorination, normally used previously, compounds can be formed that resist biological oxidation (9). An example of this is given by the following studies in the Dohne waterworks of Rheinisch-Westfälischen Wasserwerke in Mülheim.

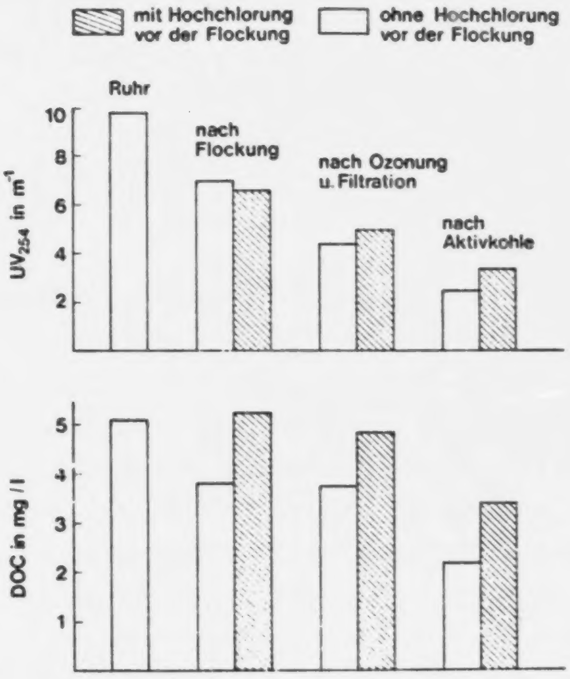


Fig. 6

Comparison of change of UV- and DOC-values at Dohne waterworks (RWW) with and without breakpoint chlorination

mit/ohne Hochchlorung = with/without breakpoint chlorination;

vor der Flockung = before flocculation;

Ruhr = river Ruhr;

nach Flockung = after flocculation

nach Ozonung u. Filtration = after ozonation and filtration;

nach Aktivkohle = after activated carbon

This diagram shows the mean values with their standard deviations, over a longer observation period, of the dissolved organic carbon (DOC) and the UV extinction (254 nm) for a method with and without break-point chlorination. Further treatment was in both cases the same and consisted of flocculation with sedimentation, treatment with ozone, and both gravel and a subsequent activated-carbon filtration.

The DOC values in particular show clearly that the high chlorination performed before the flocculation and sedimentation reduces the activity of the flocculation plant and of the activated-carbon filter. The same is true for the subsequent soil filtration.

These results explain, as do many other findings, why more detailed attention has been paid to the processes involved in the chlorination of water in recent years.

Advantages and disadvantages of chlorination

The oxidation with chlorine started to be introduced into drinking water treatment roughly around the middle of the last century though even then it was a controversial subject, and in the last 50 years became the most commonly used oxidation method. This is because chlorination has some important advantages, which are contrasted with its disadvantages in the following table. (Table 9)

With chlorine used in the correct quantities reliable disinfection is always achieved. It is simple to meter out the chlorine and the investment costs are reasonable. Chlorination also allows the preservation of a residual chlorine content in the distribution network. With the oxidation of ammonia to gaseous nitrogen, which is possible even at low temperatures, high chlorination also effects the removal of unwanted material, the concentration of which has risen strongly in the last 25 years in many effluent-loaded

TABLE 9 ADVANTAGES AND DISADVANTAGES OF CHLORINATION

Oxidation with Chlorine	
Advantages	Disadvantages
Reliable disinfection Low investment costs	Occassionally large additional amounts required
Easy to meter out, simple to control	Danger of chlorine gas in case of accidents
NH_4^+-oxidation up to nitrogen at breakpoint-chlorination Residual amount in distribution network	Formation of organo-chloro compounds which may be health hazards

surface waters. When we look at the historical development of the process we find, surprisingly, that the first works and patents on chlorination were concerned above all with the oxidizing action of chlorine and with the possibility of removing organic impurities in drinking-water treatment. From this point of view we can see why already before the turn of the century the question was asked whether it was right to use such a strong oxidizing agent as hypochlorite for drinking-water treatment. It was thought that it might be better to do without strongly contaminated raw water than to treat it with very large amounts of chlorine and supply this to the consumer.

This cry for "naturally pure" water would certainly have been much more urgent if what we know today as a result of our considerably improved analytical possibilities had been known then. When chlorination is applied to organically loaded water, especially by reaction with humic acids, large quantities of organic chlorine compounds are formed, the best known of which are the haloforms, whose distribution in drinking water in Canada according to a recent publication is shown in the following figure (10).

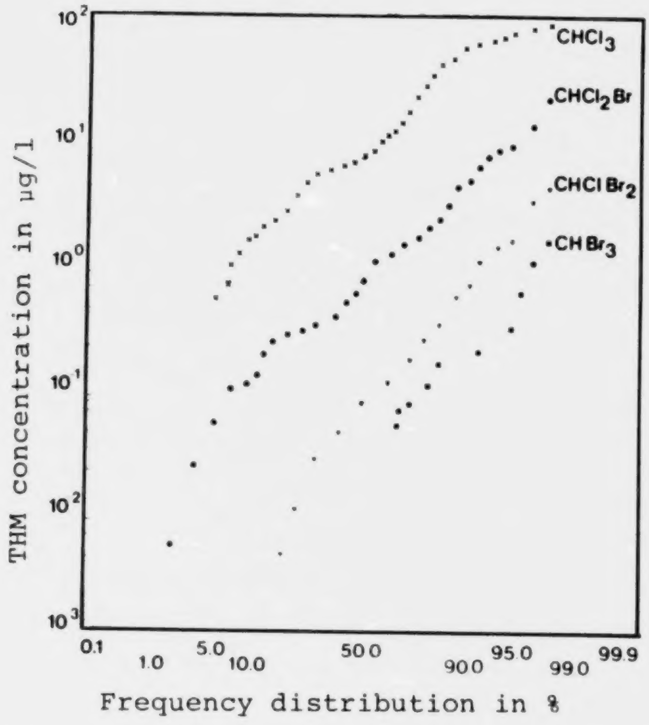


Fig. 7 Frequency distribution of trihalomethane concentrations in treated water (from: National survey for halomethanes in drinking water, Canada 1977)

The frequency distributions of the measured concentrations shown in the figure are somewhat more favourable than the corresponding values for the United States. However, the values are rather higher than the ones measured by our Institute in Central Europe, i.e. in the German Federal Republic and Switzerland. Relevant information on this is contained in the following figure.

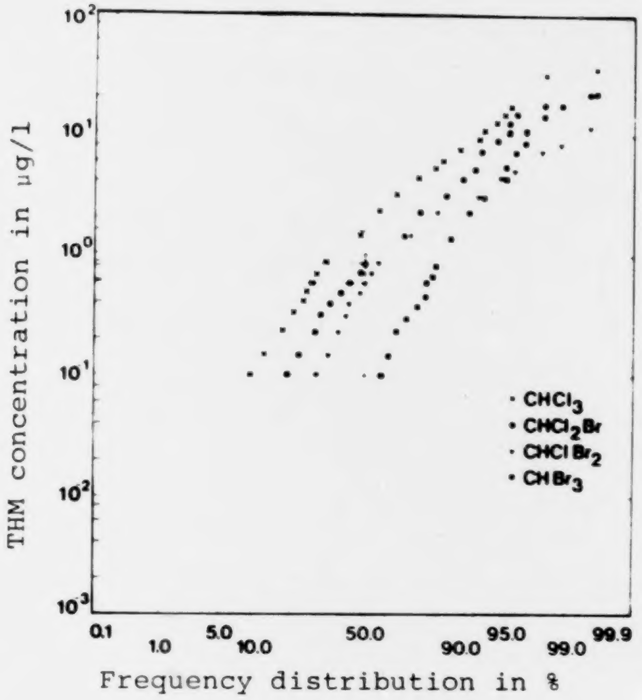


Fig. 8 Frequency distribution of trihalomethane concentrations in drinking waters in the Federal Republic of Germany and Switzerland

What is particularly important, and it makes a general statement very difficult, is that even in the case of approximately similar waters the values show very large scatter, though the causal connections cannot be clearly explained. This is also shown by the results reproduced in the following figure, which come from the above-mentioned work of the Canadian Ministry of Health.

This figure shows the trihalomethane concentrations of various waters in Canada in dependence on the chlorine demand, i.e. in dependence on the chlorine consumption. The

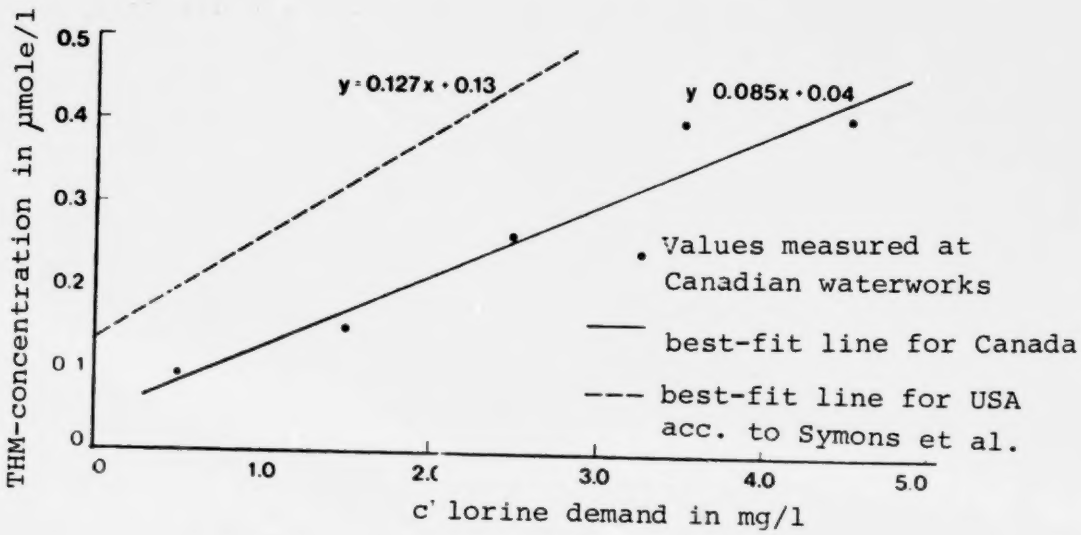


Fig. 9 Dependence of trihalomethane formation on the chlorine demand, according to measurements made in Canada and the United States

large scatter range of the data can be clearly seen, and it is clear why similar measurements in the USA lead to a different best-fit line than the Canadian studies.

As already mentioned at the beginning of this paper, the volatile chlorine compounds constitute only a small part of the total organic material formed during chlorination, as shown in the following table.

These results were obtained with Neckar water in the Technical Works in Stuttgart within the framework of a BMFT research programme. It can be seen that the values of the dissolved organic chlorine (DOCl) are greater by a factor of 10 - 20 than the trihalomethane concentrations, and furthermore, that it is extremely difficult and expensive to remove the chlorine compounds from the water, e.g. by activated carbon, once they have been formed.

TABLE 10 EFFECTS OF CLASSICAL TREATMENT FOR A RIVER WATER (NECKAR, STUTTGART) WITH BREAKPOINT CHLORINATION AND ACTIVATED CARBON FILTERS

	River water	After breakpoint chlorination, flocculation, sedimentation and filtration	After GAC Carbon LSS	After GAC Carbon F 300
Dissolved organic carbon (DOC) mg/l	5.0	4.1	3.1	1.6
UV absorbance at 254 nm m^{-1}	10.9	8.6	5.0	3.6
Sum of haloforms µg/l	0.4	50	16	25
Total organic chlorine (TOCl) µg/l	33	524	364	296

However, such measurements must not automatically lead to the conclusion that chlorine should in general be abandoned as an oxidizing agent. If stepwise chlorine oxidation is used, in place of the break-point chlorination common up to now, then from the beginning much lower concentrations of chlorine compounds are formed and a considerably better purification effect is obtained, particularly with activated-carbon treatment.

Stepwise chlorination means that before the flocculation and activated-carbon filter only so much chlorine is added, and even then intermittently if possible, that no free chlorine is present over a longer period. For this purpose the amount of chlorine must be kept well below the break-point, as shown in the next figure.

For every gram of chlorine introduced considerably lower haloform and DOCl concentrations are then produced, the reaction time also being significant.

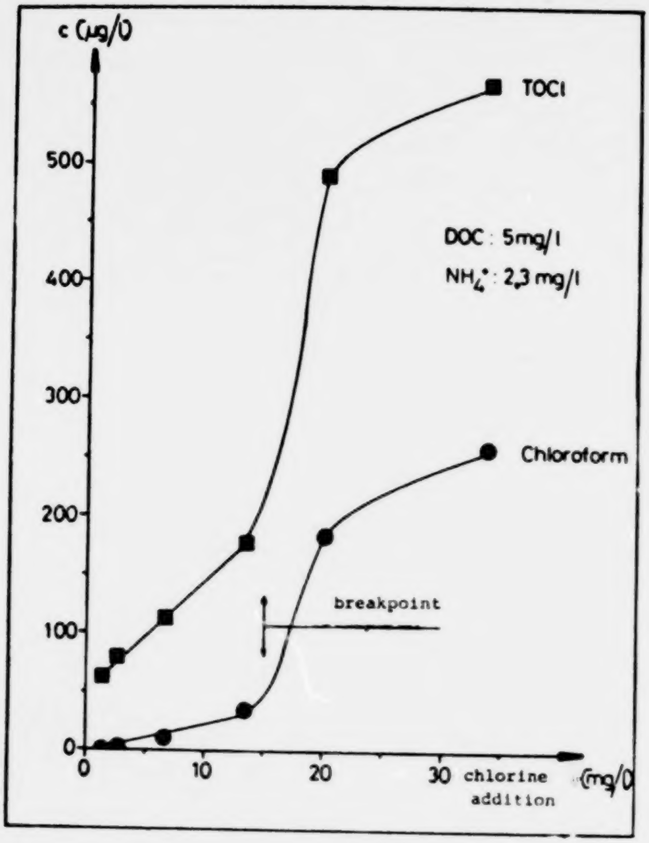


Fig. 10
Concentrations of chloroform and TOCl as a function of the initial concentrations of chlorine after a reaction period of 20 h

This is an impressive example of the fact that the undesirable effects of this oxidation stem not from the type of the oxidizing agent itself but from the conditions of its application. In oxidation processes in particular there are nearly always certain optimal doses of the oxidizing agent, and doses exceeding this optimum are sure to have unwanted results.

From the point of view of naturally pure waters it is also incorrect to attempt to eliminate the disadvantages of a water containing too much organic material simply by adding larger amounts of chlorine. If the relationships are properly considered and the right combination of purification methods is chosen, then in spite of the apparently great advantages of ozonization, chlorination can and will continue to be used successfully for the oxidation and disinfection in drinking water treatment.

Advantages and disadvantages of oxidation with ozone

The preceding outline of oxidation with chlorine has shown that the principal disadvantages of this oxidizing agent appear when the chlorine is added to the raw water before flocculation and when the amount added is so large that a concentration of free chlorine is maintained for a longer time. This type of procedure is called break-point chlorination and it is most frequently used in the classical process scheme for the treatment of drinking water. This is shown in the next figure on the extreme left.

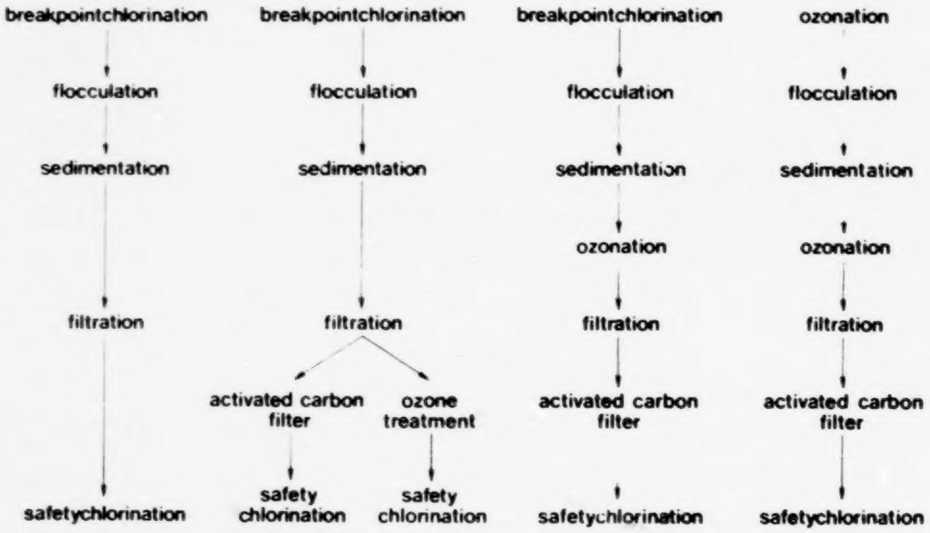


Fig.11 Process scheme development for river-water treatment in Europe (without underground passage)

In Europe this simple scheme began to be supplemented 10 - 20 years ago, in such a way that the excess chlorine and part of the chlorine compounds formed were removed in an activated-carbon filter (11). The disadvantage of this is the rapid exhaustion of the carbon filter as regards adsorption but not as regards dechlorination. Therefore processes have been favoured, especially in France, in which instead of adsorption another oxidation is carried out, but this time with ozone in place of the chlorine (12). This procedure is particularly effective in the removal of undesirable odours. However, with many waters relatively large amounts of chlorine are required for the subsequent safety chlorination if a repopulation of the water with bacteria in the distribution network is to be avoided.

This disadvantage is not observed in the last but one cited process scheme, which was first used successfully in Langenau waterworks of the Stuttgart water supply (13). Here ozonization is carried out after flocculation and sedimentation and before filtration. This type of process has the advantage, if the initial amount of chlorine is not too large, that biological processes are set up in the activated-carbon filter, leading to a longer filter running time.

Because of the otherwise too great disadvantages due to break-point chlorination, this process is limited to waters whose organic loading is not too high. For this type of water, e.g. as is found in the lower Ruhr in Mülheim, the use of ozone treatment alone is more suitable, with a preliminary ozonization before flocculation and a main ozonization stage after sedimentation and before filtration. A detailed plan of this plant is given in the next figure.

The initial addition of ozone takes place in a mixing chamber together with the addition of the flocculation agent, with very high turbulence and a short reaction time. This type of pre-treatment promotes the subsequent flocculation, which in this case is performed in a pulsator. Then follows the main ozonization stage and the gravel and activated-carbon

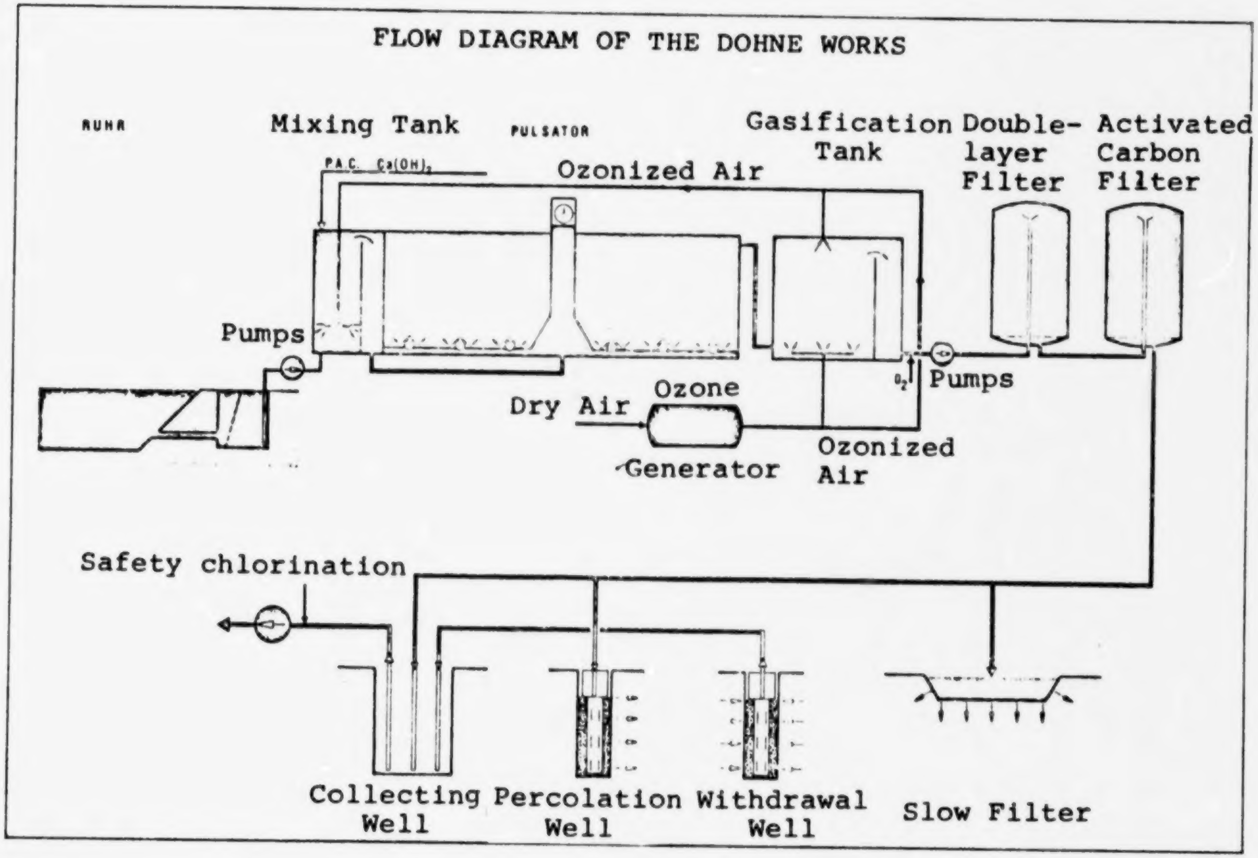


Fig.12 Flow scheme Dohne-Mülheim waterworks

filtration. The mechanical, biological, and adsorptive purification in the filters, enhanced by the ozone, is concluded in a soil passage - more of which later on.

This complicated but nonetheless very effective procedure for the use of ozone as an oxidizing agent is necessary because ozone has one disadvantage that must be considered.

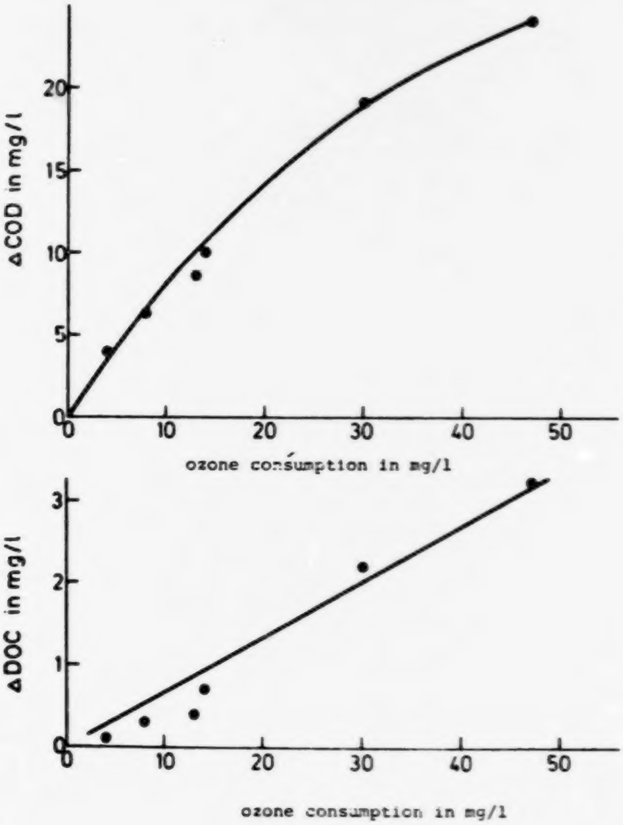


Fig.13 Decrease of DOC and COD in dependence on the ozone amount

Both the COD and the organic carbon are decreased by it. However, even with large amounts of ozone the efficiency is low, which is undesirable from the economic point of view. Ozone only transforms the organic materials and by itself cannot remove them completely.

Therefore, an ozone oxidation within the framework of drinking-water treatment can only be successful when one of the effects compiled in the following table is aimed at.

TABLE 11 EFFECTS OF OZONE TREATMENT

Disinfection;
Virus inactivation;

Microflocculation;
Formation of precipitable organics;

Transformation of resistent into biodegradable substances;
Promotion of bacterial growth;

Decrease of molecular weight of organics;
Increase of polarity of organics;

Destruction of aromatic substances;
Removal of hetero-atoms;

Disinfection and virus inactivation are among these effects. Microflocculation and an improved precipitation of the organic substances can also be attained.

Essentially more important is the improvement of biological degradation by ozonization, described by many authors, which is due jointly to the decrease in the molecular weight and the increase in the polarity of the organic substances. As already stated, the latter also has a beneficial effect on the corrosion behaviour.

In contrast to these advantages of the action mechanism, there are also the following disadvantages, shown here together with other positive factors.

TABLE 2 ADVANTAGES AND DISADVANTAGES OF OZONE IN DRINKING-WATER TREATMENT

Oxidation with Ozone	
Advantages	Disadvantages
Rapid disinfection and virus inactivation	High ozone consumption by organic substances
No commercial chemicals required	High investment- and operating costs
Microflocculation Formation of degradable organic substances	After-treatment step and installation required
Increase of polarity Transformation of resistant into biodegradable substances No formation of harmful substances	Decrease of molecular weight Increased germ formation in distribution network Biological after-treatment and safety chlorination required
Numerous processes and installations for ozone input	Difficult to control Mass transfer often determines ozonation efficiency

There are therefore cases in which particularly the raw water has a high ozone consumption. In such cases the already high costs of investment and operation become really disadvantageous, even when no commercial chemicals are required and no residual substances from the ozone are left over at the end of the oxidation.

Furthermore, ozone can only be used in a few waters without some after-treatment, and here the problem of what processes and installations should be used to bring about the necessary contact between the ozone and the water constituents is much more complicated than in the case of the other oxidizing agents. The mass transfer and the associated relationships determine to a very large extent the ozonization efficiency.

Since this problem often receives insufficient attention, although it is of great significance for optimizing the use of ozone, there are some further points that should not go unmentioned.

First, selection of the correct dosage in a much more significant factor for ozone than for the other oxidizing agents. This is illustrated by the following figure from a work by Dr. Kurz of our Institute (14).

This shows the change in a hymatomelanic acid, i.e. a humic acid of medium molecular weight, as a function of the ozone addition in mg of ozone per mg of the acid. The flocculation effectiveness was studied.

It can be seen that small additions will primarily impair the flocculation efficiency, which is ascribed, among other causes, to the decrease of the molecular weight.

With larger ozone additions the increase in polarity due to the increased number of carboxyl groups is the predominant factor. The humic acid as a polycarboxylic acid is thus converted into an anionic polyelectrolyte, causing a clear improvement of the flocculation. This reaches its maximum at a certain dose of ozone, since from this point on the decrease of the molecular weight, which continues as the amount of ozone added is increased, becomes the predominant factor.

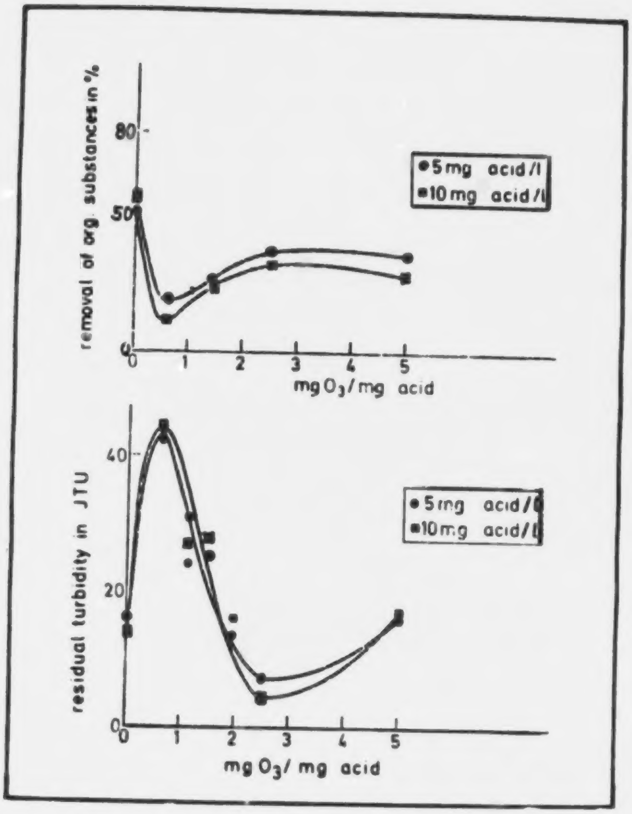


Fig. 14

Residual turbidity and removal of organic material at various ozone dosages (100 mg kaolin/l and 5 mmole $CaCl_2$/l)

The flocculation optimum is fairly clearly marked in this case. However, it is not easy to achieve this optimum for every composition of the organic water constituents. Also, the magnitude of the ozone addition is not the only important factor, but also the nature of the addition, as has been clearly demonstrated by Lienhard in recent studies at our Institute. To clarify these relationships some of the results thus obtained are shown in the next figures.

In this representation the experimental results are plotted on the decrease of UV extinction of humic acid from Lake Constance with various doses of ozone. The ozone was added to the water in the form of a concentrated solution, either all at once or gradually in five portions. It is clear that the stepwise addition has a better effect in lowering UV extinction if larger amounts of ozone are added, while the opposite is true for very small additions.

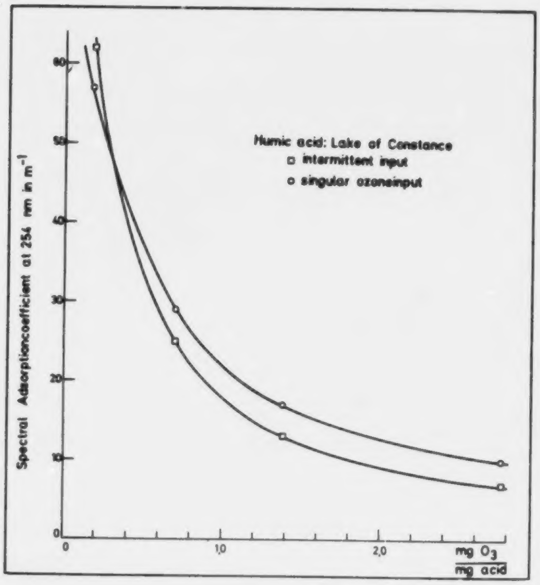


Fig. 15

Spectral absorption coefficient in dependence on ozone amount, with various doses of ozone

This effect is even more marked in the case of humic acid from Ruhr raw water, as can be seen from the following figure.

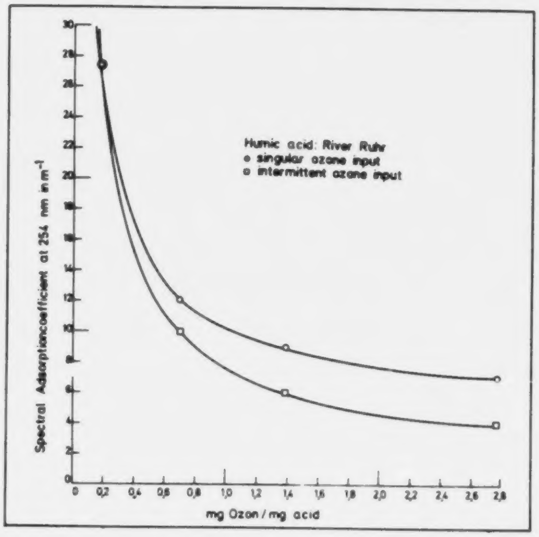


Fig. 16

Spectral absorption coefficient in dependence on ozone amount, with various doses of ozone

The reason for these differences lies in the somewhat different molecular-weight distributions for the two natural humic acids.

The same effect becomes even clearer when after the ozonization a flocculation is carried out, where with relatively high initial concentrations a more than 30% better effect can be obtained in the case of the stepwise addition.

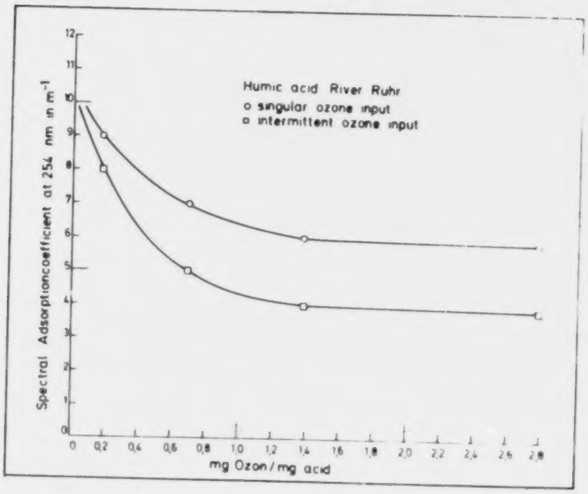


Fig. 17
Spectral absorption coefficient after ozonation and flocculation in dependence on the ozone amount, with various doses of ozone

The changes that occur in both cases can also be seen when the molecular-weight distribution is considered. They are reproduced in the next figure.

The reduction of the mean molecular weight in both cases is apparent, together with the fact that the effect is somewhat greater in the case of the stepwise addition. It may therefore be assumed that the relative number of carboxylic groups is also more strongly increased by the stepwise addition of ozone, and that this is the reason for the better efficiency.

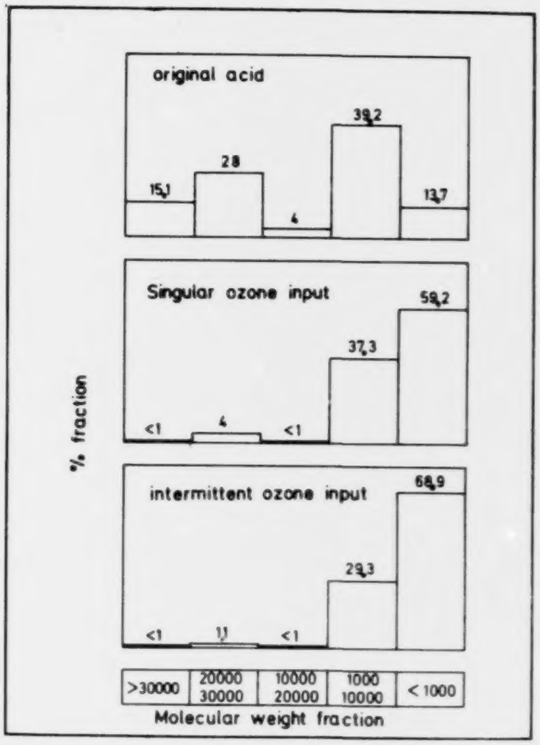


Fig. 18
Molecular-weight distribution in dependence on the ozone input

This supposition is supported by the adsorption isotherms on polar $CaCO_3$, on which more strongly polar compounds are better adsorbed. The corresponding results for two different amounts of ozone are shown in the following figure.

It can be seen that the isotherms for the stepwise or intermittent treatment are further to the left and therefore in a more advantageous position. As was discussed in detail in the earlier part of the paper, this has an effect on the precipitation kinetics of $CaCO_3$ and on the oxidation rate of Fe^{+++} ions, improving the corrosion behaviour. This improvement was clearly demonstrated for Lake Constance Water.

However, the beneficial effect of the stepwise or slow addition of ozone, when a low concentration is maintained over a longer time, is not beneficial for the whole range of

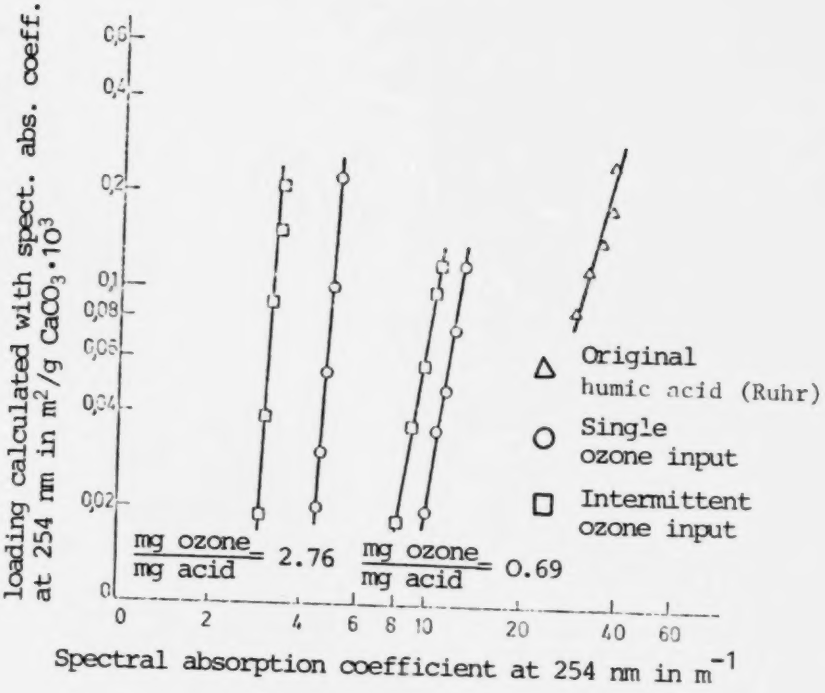


Fig.19 Adsorption of humic acid from river Ruhr on $CaCO_3$ in dependence of ozone input, with two different ozone doses

applications and actions of ozone. For example, as can be deduced from the following figure, (see Fig. 20), the situation for an effective virus inactivation is more favorable when comparatively high ozone concentrations are maintained over a relatively short time, i.e. when the ozone is added not in stages but all at once.

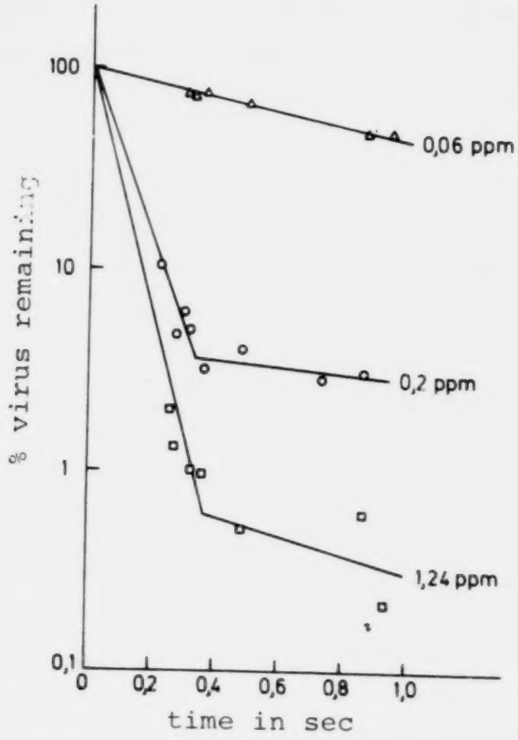


Fig. 20
Polio virus-1-
inactivation
with ozone

In this context it should also be noted that not all types of addition devices are suitable for maintaining certain concentration relationships desired in individual cases. Precise examination of the discussed relationships is therefore very important for optimal utilization of the ozone. In the comparative analysis of literature reports on ozone activity too these relations must be borne in mind. Some of the contradictory results of trials carried out at various places are due less to the different composition of the organic water constituents than to the different methods of introducing the ozone.

The fact that the influence of the material transport conditions, and hence of the mode of addition, is strongly expressed particularly in the case of ozone is due not only to the very low ozone concentration in the gas, i.e. in the oxygen or air before the passage through the ozone input system but is also connected with the chemical reaction mechanisms known for the ozone conversion, the rates of which are influenced by the ozone concentration in the water to different extents. Insofar as this is true, studies on the reaction mechanism in the use of oxidation processes are of major practical significance.

While in the oxidation with chlorine the true oxidation reactions compete with reactions leading to the formation of organic chlorine compounds, in ozonization we distinguish between the radical reaction on the one hand and ozonolysis on the other (15). Since these two different mechanisms are also dependent on pH, on some inorganic water constituents such as bicarbonate ions, and of course also on the structure of the organic water constituents, it is not surprising that very different effects of ozone treatment are observed with different waters (16).

Although general regularities are difficult to formulate, both in the case of chlorination and in ozonization a rapid addition of the oxidizing agent promotes disinfection, because high concentrations over a short period are required for this purpose. On the other hand, a slow addition over a longer time has a beneficial effect as regards the desired oxidation reactions. This fact and the appropriate incorporation of the oxidation process into the total scheme of treatment should be considered if the oxidizing agent is to be used to optimal effect in the treatment of drinking water.

Biological oxidation processes

The complex relationships in the use of chemical oxidizing agents indicate why biological oxidation processes always were, and still are, preferred in drinking-water treatment wherever they are feasible. Here passage through soil has the greatest practical significance; as the next figure shows,

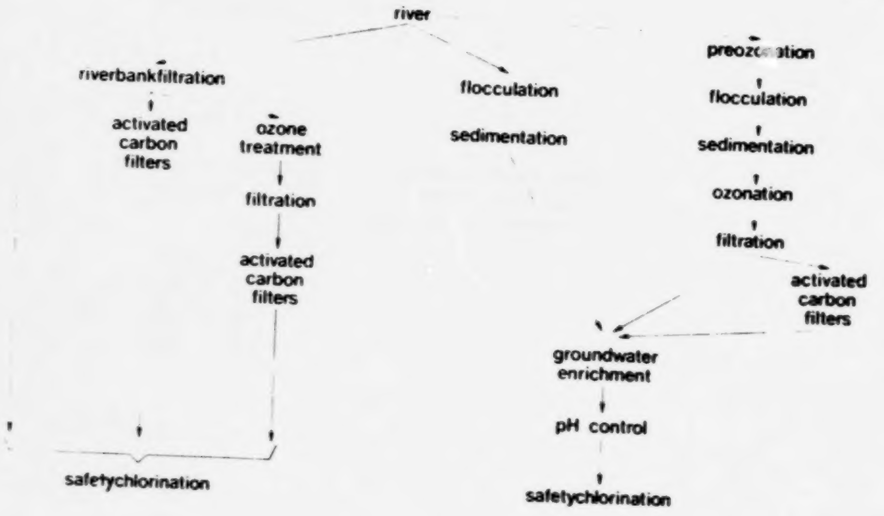


Fig.21 Process scheme development for river-water treatment in Europe (with underground passage)

a soil passage can be included in various ways into the overall treatment scheme. One possibility is the use of river bank filtration as the biological step in the process (shown on the left in the figure), combined simultaneously with the removal of suspended particles as well as colloids, and hence also the elimination of bacteria and viruses. The other possibility is ground water enrichment, such as has been practised in the Ruhr or in the dunes in Holland for many decades. In this case a preliminary treatment is necessary for the more severely polluted waters, a whole series of possibilities being available, only two examples of which are shown in the diagram.

The excellent efficiency of these processes is shown in the following table on the example of bank filtration in the Lower Rhine.

Here the values averaged over 2 years are shown, as measured in the Hamborn waterworks of NGW. The good purification

TABLE 13 Removal efficiency of riverbank filtration in Duisburg (values for 1975-1976)

		Mean concentration in the River Rhine (dissolved compounds)	Removal efficiency in percent
Dissolved organic carbon	(DOC)	7.0 mg/l	60 – 75
Adsorbable organics		4.5 "	30 – 50
Organic chlorine	(DOCl)	0.12 "	30 – 40
Organic sulfur	(DOS)	0.11 "	20 – 30
Chromium	(Cr)	6 – 12 µg/l	90 – 95
Copper	(Cu)	15 – 35 "	70 – 80
Zinc	(Zn)	90 – 250 "	40 – 60
Nickel	(Ni)	10 – 15 "	40 – 60
Lead	(Pb)	9 – 20 "	40 – 60
Arsenic	(As)	4 – 8 "	30 – 60
Mercury	(Hg)	0.1 – 0.6 "	30 – 60
Cadmium	(Cd)	0.5 – 2 "	20 – 50
Selen	(Se)	0.5 – 2 "	0 – 20

effect on the dissolved organic substances can be seen by the high efficiency of DOC reduction. The greater part of the heavy metals is also well retained, the data given referring only to the dissolved metal ions. The purification action of bank filtration on the adsorbable organic materials is much less favourable. Particularly poor effects are as a rule observed for the organic chlorine and sulfur compounds, and it is among these that many anthropogenic unwanted compounds are found, which should not be allowed to remain in drinking water.

The limits of purification effectiveness of biological processes can also be seen by considering the situation in Holland and the infiltration into the dunes, widely practised there. The following figure shows diagrammatically a plant of this kind in the Amsterdam waterworks.

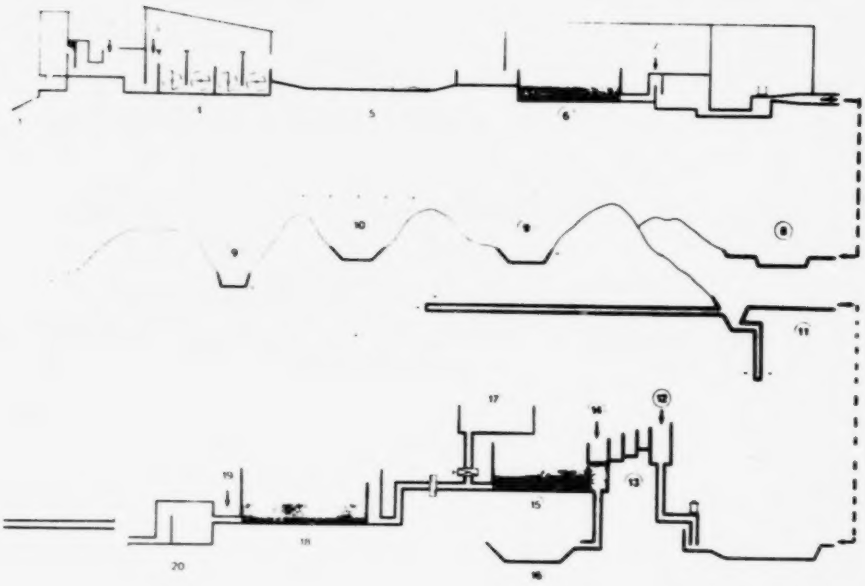


Fig.22 Process scheme of dune waterworks Amsterdam

(1) Rhine canal
(2) $FeCl_3$ dosing
(3) NaOH dosing
(4) Flocculation basin
(5) Sedimentation basin
(6) Rapid filter
(7) Chlorine dosing
(8) Distribution basin
(9)+ Percolation gullies +
(10) Collection canals

(11) Collecting basin
(12) NaOH dosing
(13) Aeration
(14) Activated carbon dosage
(15) Rapid filter
(16) Silt deposit
(17) Wash water reservoir
(18) Slow sand filter
(19) Chlorine dosing
(20) Chlorine contact basin

According to this figure, in the case of heavy pollution of the Rhine water in Holland it is necessary to perform a flocculation, sedimentation, and filtration before the infiltration; the water also needs an additional treatment after the infiltration, which will not be considered here in greater detail.

The effectiveness of the infiltration is satisfactory as regards the heavy metals and the ammonium but this cannot be said of the total organic matter present in the water.

TABLE 14 ANALYTICAL DATA FOR THE DUNE-WATER TREATMENT, AMSTERDAM 1976

		river water Rhine	before Dune-filtration	after Dune-filtration	drinking water
DOC	mg/l	7.1	5.4	4.1	3.6
Colour	mg Pt/l	28.0	15.0	11.0	8.
Threshold number		32.0	5.0	—	0
Hydrocarbons (oil)	mg/l	0.26	0.03	—	0
Chloride	mg/l	215.0	227.0	178.0	174.0
Bicarbonate	"	162.0	158.0	194.0	201.0
Ammonia	"	1.5	0.2	<0.05	<0.05
Nitrate	"	17.0	20.0	5.5	5.8
Phosphate	"	1.2	0.2	0.1	0.1
Iron	µg/l	1600.0	100.0	50.0	20.0
Chromium	"	35.0	<1.0	<1.0	<1.0
Copper	"	22.0	8.0	5.0	5.0
Zinc	"	150.0	25.0	15.0	10.0
Cadmium	"	2.9	0.2	0.1	0.1
Mercury	"	0.5	0.1	<0.1	<0.1
Lead	"	28.0	3.0	3.0	2.0

This is in part due to the fact that the fraction of materials that are difficult to degrade biologically is relatively high in the Rhine in Holland. However, it is also due to the fact that the conditions for biological degradation as regards the residence time and the medium are not quite as good in the dunes as on the river banks used for filtration.

From this point of view it is also understandable that the processes in which the biological purification is not carried out underground but in industrial installations have a limited efficiency. This is true above all when slow filters are used by themselves. In this process, although really good results are obtained in the uppermost layer, the residence period in the subsequent 1 - 2 m thick layers of sand is too short for further extensive purification. The following figure is a good example of this phenomenon, showing the results obtained in the infiltration of pre-purified waste water in the Dan region in Tel Avia, Israel (17).

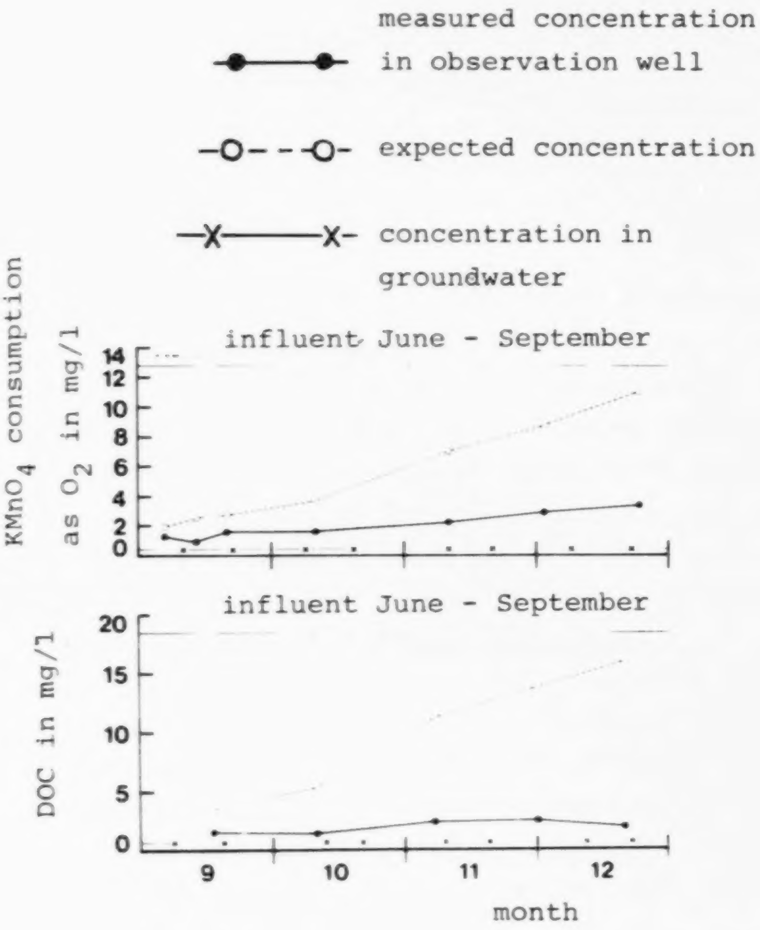


Fig.23 Expected and measured concentrations of organics in pretreated wastewater after 3 months' residence time underground (Dan Region Sewage Reclamation Project, Tel Aviv, Israel)

The upper part of the figure gives the purification effects of the upper 2 m of sand as regards the COD and the permanganate consumption. It can be seen that about 25% of the dissolved impurities are removed.

The lower figure contains the values after 3 months' residence time underground. In addition to the mean values of the raw water before infiltration and the ground water values, the figure gives the effective numerical values measured after the soil passage and the data that would be expected if no degradation had taken place.

This clearly demonstrates the great advantages of a long residence time underground. The over-all efficiency is about 75% and the residual contents of organic substances are quite acceptable. It can also be seen that for part of the material the biological degradation requires a relatively long time or that it is incomplete.

This process is also the key to the special effectiveness of activated-carbon filters in the biological purification of water. As a result of their adsorption on the activated carbon the organic materials remain in the filter for the long time required for the biological oxidation of a number of substances. The materials must of course be adsorbable, and subsequently they have to be available for degradation, i.e. they must be desorbable again.
The last example shows that really astonishing results can be obtained in such filters.

This refers to trials carried out by BASF in collaboration with our institute. The figure shows the experimental plant, which consisted of an activated-carbon filter through which was circulated waste water from the BASF biological purification plant with intermediate aeration. As a result of this process, the next figure shows, surprising purification effects

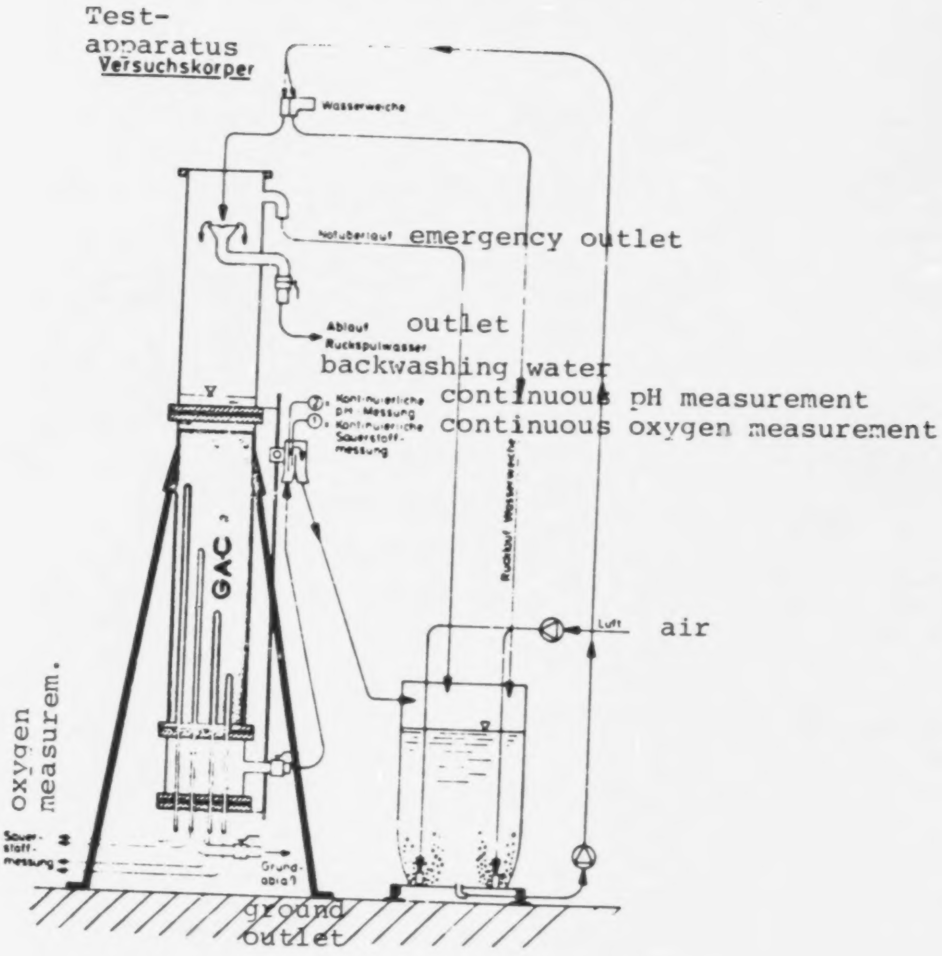


Fig.24 Biological purification plant of BASF (Badische Anilin- und Soda-Fabrik, Ludwigshafen)

of over 90% are produced with respect to the organic carbon. The filter has been running for about 18 months without any apparent reduction of this purification efficiency.

For the evaluation of the treatability of this waste water in drinking-water treatment this result means that nearly all the organic material still present in the discharge of the BASF clarification plant is removed without major

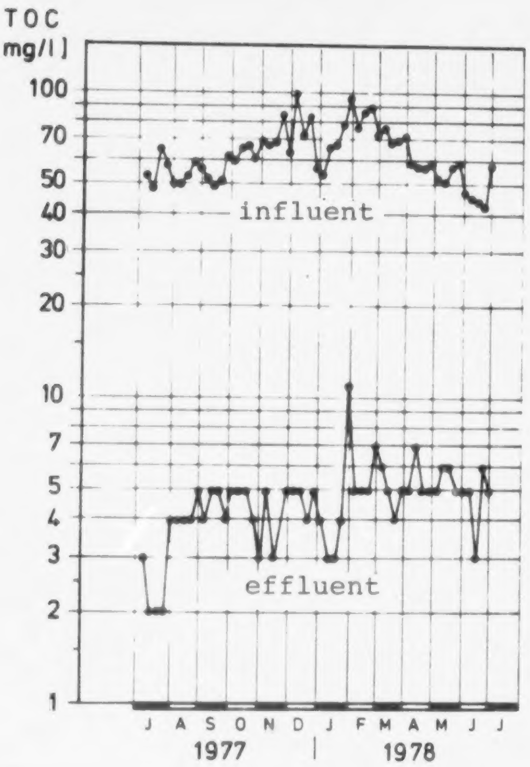


Fig. 25
TOC-degradation in the biological purification plant of BASF (Badische Anilin- und Soda-Fabrik, Ludwigshafen)

problems in the waters and in the drinking-water treatment, and that consequently the risk to the drinking water supply due to wastewater is negligible.

It would be desirable if a similar testing of the waste water constituents for the risk they present to drinking water were also carried out in other clarification plants, and if the results were applied to intra-works purification and waste water treatment measures in works where there are high proportions of organic substances which are difficult to degrade biologically and which impede biological purification.

For the sake of completeness it should further be mentioned that with the low loading chosen here quite similar effects can be obtained, so that the use of activated carbon is only advantageous here at higher loadings or still lower initial concentrations.

In any event, the example illustrates the outstanding purification capacity of natural biological processes, and the results explain why such value is placed on processes of this kind in Central Europe and especially here in the Rhine catchment basin.

Nevertheless, these methods also have their disadvantages, as can be seen from the next table.

TABLE 15 ADVANTAGES AND DISADVANTAGES OF BIOLOGICAL PROCESSES FOR DRINKING-WATER TREATMENT

Advantages	Disadvantages
Low operating costs	Large space requirement
Simple operation	Small possibilities of intervention
High efficiency	Susceptible to toxic substances
Automatic adaptation to changed conditions	Adaptation is very slow in many cases

In this respect special mention should be made of the large space requirement, the small possibilities of intervention in cases of perturbations and their disadvantageous effects. For this reason the drinking water supply is compelled to make appropriate demands on the water protection. From this point of view I personally consider continuous monitoring of waste-water purification with the aid of a biological process such as the BASF operate to be more important than e.g. the performance of fish tests in which acutely toxic waste-water constituents in greater concentrations, at the most, have been found. These normally inhibit the biological purification so strongly that they can be recognized.

With these details on the significance and application of biological purification processes this introductory report comes to an end. The considerations and results presented in it will be amplified in many respects in the course of the conference by means of detailed reports on individual problems from the sphere of the application of oxidation processes to the treatment of drinking water. The essential points, which may already be inferred from the examples and discussion, may be summarized as follows:

Summary

1. Oxidation processes constitute an important and often indispensable measure in the reliable production of safe drinking water.

2. A factor common to all oxidation processes is that in spite of their beneficial action they may also exert adverse effects on the quality of drinking water, especially when inappropriately applied.

3. In this connection the formation of organic chlorine compounds is of particular importance. However, these disadvantages can be avoided if the chlorine is used suitably, e.g. by stepwise addition.

4. Process-technological aspects must be considered above all if the oxidation methods are to be used to optimal effect. This applies both to the type of the oxidizing agent addition and to the appropriate inclusion of the process in the overall treatment scheme.

5. The natural biological purification processes are currently of particular importance in obtaining unimpeachable drinking water by the treatment of surface waters. Their use places certain requirements on the composition of the raw water. These aspects should be particularly considered in the future treatment of waste water and be checked by suitable test methods.

6. Optimal introduction of oxidation processes into the treatment of drinking water requires an exact knowledge of the reactions taking place and of their interrelationships. It is the aim of this conference to review the necessary knowledge in summarized form.

(1) ROOK, J.J.
Formation of Haloforms During Chlorination of Natural Waters
Water Treatm. Exam. 23 (1974), 234-243

(2) SYMONS, J.N. et al.
Preliminary Assessment of Suspected Carcinogens in Drinking Water
Interim Report & Report to Congress USEPA, Washington, June 1975, December (1975)

(3) SANDER, R., KÜHN, W., SONTHEIMER, H.
Untersuchungen zur Umsetzung von Chlor mit Huminsubstanzen
Z. f. Wasser- und Abwasser-Forschung 10 (1977), 5, 155-160

(4) -
Save Drinking Water Act, Public Law 93-523, July 9 (1976)

(5) -
Verordnung über Trinkwasser und über Brauchwasser für Lebensmittelbetriebe (Trinkwasser-Verordnung) 31 Jan. 1975
Bundesgesetzblatt (1975), I, 453-461, 679

(6) DIN 2000
Zentrale Trinkwasserversorgung
Leitsätze für Anforderungen an Trinkwasser, Planung, Bau und Betrieb der Anlagen
Deutsche Normen DK 628.1.033 Nov. 1973

(7) RUDEK, R., SONTHEIMER, H.
Einfluß natürlicher Wasserinhaltsstoffe auf die Ausfallsgeschwindigkeit von $CaCO_3$
Vom Wasser 47 (1976), 421-431

(8) SONTHEIMER, H., WÖLFEL, P.
Amelioration de la dĝradation biologique des eaux rêsiduaires par un traitement à l'ozone
Tagungsbericht: Internationaler Ozon-Kongress Paris 4-6 Mai 1977

(9) SONTHEIMER, H., HEILKER, E., JEKEL, R.M., NOLTE, H., VOLLMER, F.
The Mülheim Process
J. AWWA 70 (1978), 7, 393-396

(10) -
National Survey for Halomethanes in Drinking Water
77-EHD-9
Information Service, Department of National Health and Welfare, Brooke Claxton Building, Ottawa K 1 A, OK 9

(11) HOPF, W.
Versuche mit Aktivkohle zur Aufbereitung des Düsseldorfer Trinkwassers
gwf-Wasser/Abwasser 101 (1966), 14, 330-336

(12) GOMELLA, C.
Ozone Practices in France
J. AWWA 64 (1972), 39-45

(13) WURSTER, E., WERNER, G.
Die Leipheimer Versuche zur Aufbereitung von Donauwasser
gwf-Wasser/Abwasser 112 (1974), 2, 89

(14) KURZ, R.
Untersuchungen zur Wirkung von Ozon auf Flockungsvorgänge
Dissertation, Fakultät für Chemieingenieurwesen, Universität Karlsruhe 1977

(15) HOIGNE, J., BADER, H.
Kinetik und Selektivität der Ozonung organischer Stoffe im Trinkwasser
Internat. Symposium Ozon und Wasser Berlin, April 1977

(16) HOIGNE, J., BADER, H.
Beeinflussung der Oxidationswirkung von Ozon und OH-Radikalen durch Carbonat
Vom Wasser 48 (1977), 283-304

(17) IDELOVITCH, E. et al.
Groundwater Recharge with Municipal Effluent
Dan Region Sewage Reclamation Project, Annual Report 1977

HYGIENIC SIGNIFICANCE OF CHLORINATION AND THE REQUIREMENTS THEREFROM

G. Müller

More than 200 years have now passed since the discovery of chlorine in 1774, and during all this time it has lost none of its importance. In earlier days attempts were often made to bind "foul effluvium", called miasma, by fumigation and so render it harmless, and shortly after its discovery chlorine gas was used in France as a fumigating agent for this purpose (1). Suitable means of disinfection were only developed after the discovery of pathogens and after the infection chain typical or specific for the spread of infections became known. In ignorance of the facts, the spread of epidemics, e.g. of cholera and typhus, via drinking water was allowed to continue up to the end of the nineteenth century. This was due to drinking untreated surface water contaminated by human and animal waste and, after the discovery of sewerage, by effluents. In the United States chlorination of drinking water was used as a means of epidemic control as early as the beginning of this century, and thereafter a sudden fall e.g. in the mortality from typhus was achieved.

In Germany, on the other hand, in the middle of the nineteenth century, following Lindley's example in Great Britain, the biological method of purification of impure river water had been adopted and slow sand-filters were built, also bringing about an abrupt reduction in the incidence of typhus. The efficacy of this measure was made particularly clear during the great Hamburg cholera epidemic in 1892. As is well known, within 2 months 17,000 people were taken ill in Hamburg, which was supplied by unpurified water from the Elbe, and 9000 of them died. In neighbouring Altona, where the Elbe likewise supplied the drinking water, the slow sand-filters built there kept the number of victims down to about 200, and these became ill not by drinking the water but by direct contact with the sick (Fig. 1). When the news of the successful use of chlorinated drinking water in the control of epidemics first reached Germany from the USA in 1910 (2), the process met with opposition. Strong objections were voiced against chemical treatment of water and an "artificially performed, simplified disinfection" of this kind. Attempts were made to hang on to the old principle that "prevention is better than cure", and raw water of unimpeachable origin was demanded, which would then be treated to become drinking water. Following the discovery of pathogenic microorganisms and the realization of the connection between drinking water from river water and drinking water epidemics, the use of ground water as a drinking water supply was started early on, since, when the upper soil layers are intact and the soil is of sufficient depth, the biological purification processes taking place in the ground

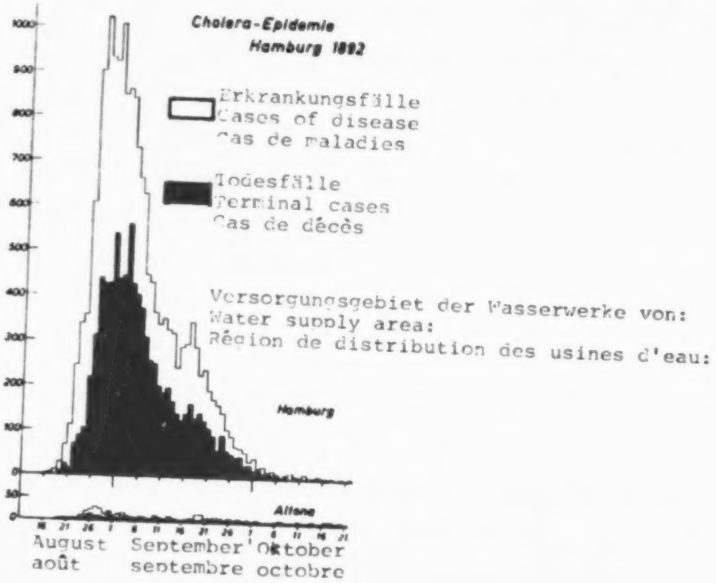


Fig. 1 Incidence of disease and deaths in the supply regions of Hamburg and Altona during the cholera epidemic

ensure a reliable protection against epidemics even without chlorination. Today this development strikes us as being retrograde. The way forced upon us - a return to surface water - is in most cases, when we consider the purifying action of the soil, taken as a short-cut, since the surface water after passing through soil, serves to enrich ground water. In this way it is still possible in Germany to draw over 90% of the water used for public supplies from genuine or enriched ground water. The direct fight with the pathogens present in unpurified surface water ceases to exist, these pathogens being further introduced via waste water, since regrettably even a well-dimensioned, mechanical and biologically working purification plant is not capable of eliminating pathogens in the purification of waste water, with the result that bacteria are still found in the treated water (3 - 5). A biological purification of waste water is therefore not a disinfection process per se. While cholera epidemics connected with drinking water no longer occur in Germany, it is only because the necessary bacteria are absent; it has so far proved impossible to prevent the incidence of typhus and paratyphus B epidemics related to the water. After the use of untreated river water as drinking water had been discontinued towards the end of the nineteenth century, these epidemics were caused exclusively by short-circuits between drinking water and waste water or between drinking water and effluent-contaminated river water.

However, in contrast to the epidemic outbreaks of the previous century, as a result of a technically faultless drinking water supply and its careful monitoring and control, short-circuits of this kind are genuine "accidents". Cases of typhus, paratyphus B, or Salmonella infections caused by such short-circuits arise very rarely directly from drinking the polluted water; an enrichment of the few bacteria present in the water must first take place in the food for the numbers necessary for infection to be reached. This was the case in the typhus epidemic in Hagen in 1955 (infection from milk cans) and the epidemic on a ship in Hamburg harbour in 1969, where water from the Elbe was used to wash dishes (7). Even within the framework of legal specifications chlorinated drinking water cannot as a rule guarantee true disinfection in the case of cross-connections with waste water or surface water, i.e. "putting an object into such a state that it can no longer infect" (8), since the organic substance introduced together with the impure water is usually sufficient to consume the chlorine before the latter can expect its disinfecting action.

Chlorine can be used in the disinfection of drinking water for the prevention and control of hygienically undesirable states, but it must be clearly understood that although the chlorination performed as so-called safety chlorination can achieve the cosmetic effect of decreasing the colony count, it hardly ever destroys pathogens after the penetration of waste water or river water into the supply system. For use as a true disinfection agent, essentially higher concentrations of chlorine are necessary than are laid down in the laws on drinking water and drinking water treatment. This is put into practice, for example, in the disinfection of new parts of the distribution network, as was also done during the 1962 Hamburg flood disaster (9), when it was only the aimed use of large quantities of chlorine that made it possible for about 1 million m^3 of Elbe water that had broken into the distribution network, and also for the pipeline system so contaminated, to be made bacteriologically safe. As a result of these aimed disinfection measures, no increase in the incidence of typhus, paratyphus B, and other salmonelloses was recorded (10).

In Germany there are many public water supply systems in which the drinking water entering the network is not chlorinated, and yet the danger of epidemics is no greater than there is from chlorinated drinking water. The chlorination of drinking water in Germany is practised for other reasons -- either to destroy the odour and taste of organic substances during the treatment or to prevent the proliferation of autochthonous aquatic flora when the appropriate nutrient media are present in the distribution network, especially in the case of long-distance pipelines, to keep to the legally prescribed limiting colony counts.

In spite of the relatively restricted use of chlorine in German public water supplies, the incidence of typhus and paratyphus B has fallen in the last 15 years, while, independently of this, the incidence of salmonelloses has risen (6). The cause of this does not lie in chlorinated or unchlorinated water but in the sector of food and veterinary hygiene (Fig. 2).

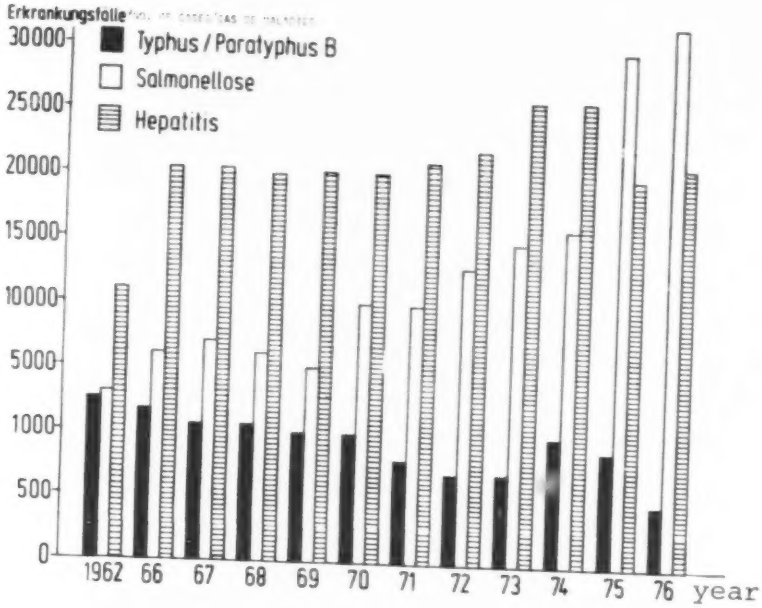


Fig. 2 Cases of typhus/paratyphus B, salmonellosis, and hepatitis in West Germany during 1962-1976

Whereas up to the end of the last century epidemics in a population were mostly of infectious origin, today diseases of noninfectious genesis are in the foreground, the most frequent being diabetes, rheumatism, cardiovascular disorders, hypertension, and cancer. In the search for the primary causes, the environmental factors must not be dismissed. Besides the air and foodstuffs, water should also play a part in this. The causal connection between water and disease was established in the majority of cases on the basis of statistics. A connection between the constituents of drinking water and cardiovascular diseases (11), and between these constituents and cancer, has therefore been obtained on the basis of statistical evidence, and certain carcinogenic substances have been identified (12). Thus, some chlorinated organic compounds (halogenated hydrocarbons), some of which had only been formed in the water as a result of chlorination, have been indicated as potentially carcinogenic. This is a recent finding and interferes with the fact that chlorine maintained its preferred position as a drinking water disinfection agent precisely because it was cheap, easy to meter out, easy to detect, and up to now regarded as harmless (13).

In contrast to other countries, in which even the waste water has been chlorinated for years, this measure has not been adopted in Germany.

The occurrence of halogenated hydrocarbons in water is therefore due in Germany to the input of industrial effluents rather than, as is the rule in America, to chlorinated domestic sewage. Since in America the cycle: (input of chlorinated sewage into the river/removal for the production of drinking water with preliminary chlorination, active carbon filtration, and post-chlorination before distribution into the network/production of waste water/waste water chlorination etc.) is relatively short and the accumulation of the halogenated hydrocarbons takes place relatively quickly, the findings there are orders of magnitude different than in Germany, especially since here the probability of the formation of chlorinated substances in high concentrations by chlorination of drinking water within the legal limits during the water distribution is relatively low.

According to American investigations (14), some of the incidence of cancer of the stomach, intestine, and liver may be related to trihalomethane exposure, especially chloroform. According to German mortality statistics (15) on the number of deaths from cancer of the stomach and of the intestinal tract (Fig. 3), a rise in the general cancer mortality rate is found from 1932 to 1974, however, a fall in the death rate from cancer of the stomach is observed, and the number of terminal cases of cancer of the intestinal tract is fairly constant. In a comparison of the numbers of death from cancer of the liver, stomach, and the urinary tract, types of cancer which, in animal experiments can be induced by chloroform, it can be seen that, within a period of 10 years (1956 - 1967) (Fig. 4), the deaths from stomach cancer have decreased, those from cancer of the liver have remained fairly constant, while those from cancer of the urinary tract have risen by about 25%. Epidemiological enquiries on this are not yet available in Germany.

The example of chlorination of drinking water shows clearly how problems of hygiene can shift in the course of a century. A measure that contributed essentially to the control and prevention of epidemically occurring, infectious diseases may now be a contributory cause of the occurrence of non-infectious diseases. The long years of success must now of necessity be weighed against considerations of a completely different kind, particularly since very little is still known about the causes of cancer due to exogenous noxae. The fact that we now possess mature and almost complete knowledge

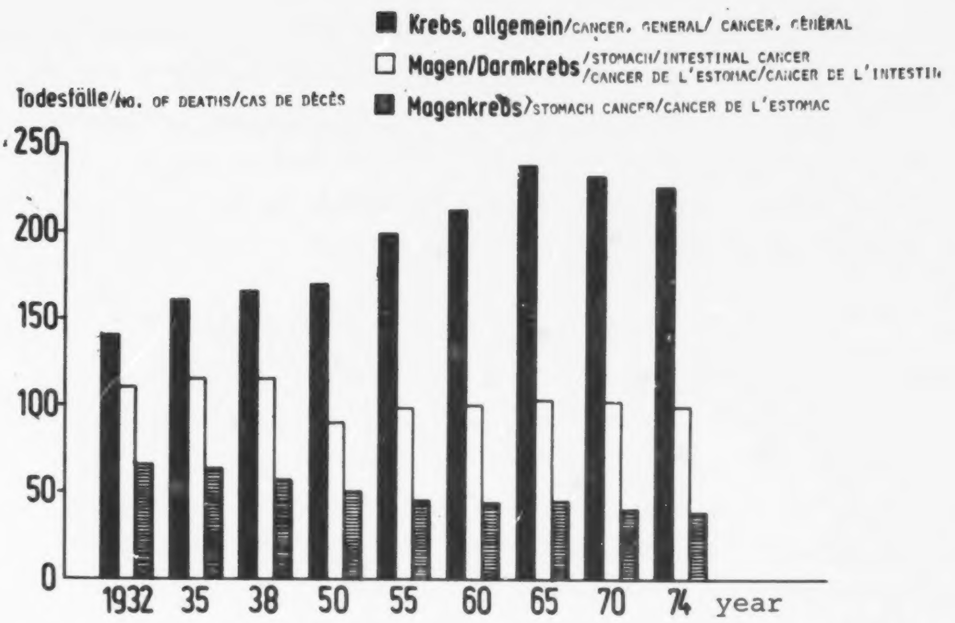


Fig. 3 Mortality due to cancer of the stomach and the intestine in West Germany from 1932 to 1974

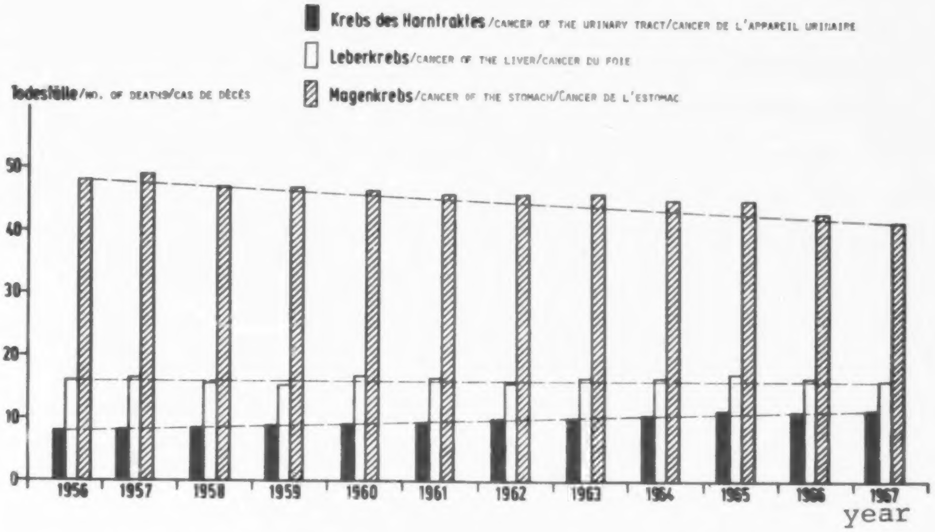


Fig. 4 Deaths due to cancer of the stomach, liver, and urinary tract in West Germany over 10 years (1956-1967)

of the epidemic pathogens stands in opposition to the difficult work necessary before we can make equally precise statements on the aetiology of cancer. This will be an essential task for the twentieth and twenty-first century, inductive epidemiology, i.e. purely empirical collection of facts and observations, playing at first a leading role.

On the basis of this inductive aetiological comprehension of environmental noxae, a series of carcinogenically acting substances has already been established. Since water is drunk every day, it is obvious that its constituents should also be included in these inductive-epidemiological investigations. However, it must be understood that an evaluation of such correlations, which have only been established statistically, is extremely difficult, since there is no doubt that cancer is rarely due to a single factor. On the contrary, many factors should be included in the evaluation, e.g. the nature and action of the carcinogen, dose, cumulation, metabolism, synergistic effects, intervention or co-carcinogenesis. The social situation of the patient also plays a part as an exogenous factor, e.g. occupation, nutrition, place of residence, living habits, disposition, and the nature and duration of the exposure to the carcinogen. Moreover, it is difficult to say whether, and under what conditions, an experimentally determined or suspected carcinogenesis becomes relevant for the whole population or for a section of the population (16), especially as the list of the known environmental carcinogens is already very long and is certainly still growing. Attention should also be paid to the ratio of the amount occurring in the environment, established by modern trace analysis, to the relatively high doses used in experiments on animals. In spite of this, it cannot be safely excluded that life-long exposure of people to one or more carcinogens may lead to a cumulation of subthreshold doses, or that an additive effect can occur, leading to a carcinoma.

As long as the relationship between chlorinated organic compounds and potential carcinogenesis, decisive for human health, remains unexplained, it seems expedient and necessary, in consideration of the present-day state of science and knowledge, to follow the ancient medical principle that prevention is better than cure and to use and perform chlorination of drinking water only when absolutely necessary.

(1) MÜLLER, R.
Medizinische Mikrobiologie
Urban & Schwarzenberg, 4. Ed. Berlin/Wien 1950

(2) REPLOH, H.
Sechs Jahrzehnte Wasserchlorung - Rückblick und Ausblick
Wasserfachliche Aussprachetagung des DVGW, Berlin 1968

(3) MÜLLER, G.
Werden Keime der Salmonellagruppe durch künstliche Abwasserreinigungsanlagen aus dem Abwasser entfernt?
Städtehygiene (1955), 106

(4) MEGAY, K.
Umwelt und Gesundheit, Fragen der Wasserverschmutzung
Vortrag 25. Jahrestagung Österr. Volksbildungswerk
April 1971

(5) MÜLLER, G.
Tuberkelbakterien im Schlamm mechanisch-biologisch arbeitender Abwasserreinigungsanlagen
Städtehygiene (1959), 96

(6) MÜLLER, G.
Water Chlorination, Environmental Impact and Health Effect
Ann Arbor Science Publishers 2 (1978)

(7) MÜLLER, G.
Wasser und Infektionskrankheiten in Bewertung von Risiken für die Gesundheit
G. Fülgraff Ed. Gustav Fischer Verlag, Stuttgart (1976)

(8) MÜLLER, G.
Grundlagen und Probleme der Trinkwasserdesinfektion
Bundesgesundheitsblatt (1969), 245

(9) MÜLLER, G.
Welche Konsequenzen ergeben sich aus den Erfahrungen der Hamburger Flutkatastrophe für die hygienische Trinkwasseruntersuchung?
Arch. Hyg. 148 (1964) 321-327

(10) DROBEK, W.
Auswirkungen der Flutkatastrophe auf die Wasserversorgung in Hamburg
VDI-Zeitschr. 104 (1962), 32, 1649

(11) MÜLLER, G.
Probleme der epidemiologischen Beurteilung von Wasserinhaltsstoffen
Schriftenreihe Verein Wasser-, Boden- und Lufthygiene e.V.
Fischer Verlag, Stuttgart 40 (1973)

(12) ALAVANJA, M., GOLSTEIN, I., SUSSER, M.
A case control study of gastrointestinal and urinary tract cancer in relation to drinking water chlorination
Water Chlorination, Environmental Impact and Health Effects, Ann Arbor Science 2 (1978)

(13) PFEIFFER, E.H.
Über die Schadwirkung der Wasserchlorung unter besonderer Berücksichtigung der Frage der Co-Cancerogenität von Chlor
Zbl. Hyg. Bakt., I. Abt. Orig. B 166 (1978), 169-184

(14) -
New Orleans Area Water Supply Study
Report EPA - 906/10-74-002, Dallas/Texas (1975)

(15) -
Das Gesundheitswesen der Bundesrepublik Deutschland
Hrsg. Bundesminister für Jugend, Familie und Gesundheit
W. Kohlhammer Verlag Stuttgart/Mainz 1 - 4 (1970)

(16) KLAND, M.J.
A priori predictive methods of assessing health effects of potential chemical toxicants and suspect carcinogens
Water Chlorination, Environmental Impact and Health Effects, Ann Arbor Science 2 (1978)

REACTION OF CHLORINE WITH INORGANIC CONSTITUENTS OF WATER

K.-E. Quentin and D. Weil

Although chlorination is performed in water treatment for bacteriological and hygienic reasons, the oxidizing properties of chlorine are also of process-technological significance, for example for the precipitation of iron and manganese and for the removal of sulphide sulphur. Other elements, in contrast, can pass into their stable oxidation states and remain in the water. An example of this is selenium, for which, on account of its toxicity, a low permissible level in drinking water, in the microgram range, has been laid down in most countries. The oxidation potential of oxygen-containing water is about 600 - 800 mV, and the selenium is then present in the neutral pH region as selenite or hydrogen selenite. The oxidation potential is raised by chlorine to about 1100 - 1200 mV, i.e. into the stability region of the selenate (Fig. 1). The relationships for surface waters which are low in oxygen or organically loaded are even more remarkable. According to our own work on nine rivers and lakes in West Germany, selenium is present partly in the elementary form, and this increases with increasing content of organic matter in the water. At total selenium contents of 0.6 - 2.4 μg/l the elementary selenium ranges between 0.25 and 1.9 μg/l, corresponding to ratios of elementary Se to SeO_3^{2-} of between 1:1 and 4:1 (cf. Table 1). While the elementary selenium may be eliminated by flocculation, this is not so effective in the case of the selenite or selenate. Arsenic, on the other hand, with consideration of the usual oxidation potentials of raw waters, is from the outset present predominantly as arsenite or arsenate (Fig. 2). It also appears necessary to pay greater attention to these effects of chlorination in the future, since we have no detailed information on the occurrence and the behaviour of individual inorganic species of such elements, especially as regards the course and the consequences of oxidative water-treatment processes.

TABLE 1 Selenium content in West German waters ug/l Se (1977)

Waters	Collection site	Total selenium	Selenite	Elementary selenium
Danube	Leipheim	1,40	0,25	1,15
	Passau	1,10	0,50	0,60
Rhine	Basel	1,20	0,65	0,55
	Cologne	1,90	0,60	1,30
	Duisburg	2,00	0,70	1,30
	Karlsruhe	1,20	0,70	0,50
Lake Constance	Sipplingen	0,60	0,35	0,25
Main	Frankfurt	2,40	0,50	1,90
Ruhr	Mülheim	1,90	0,50	1,40
Fulda	Kassel	1,45	0,45	1,00
Weser	Bremen	1,60	0,35	1,25
Elbe	Hamburg	2,20	0,75	1,45
Neckar	Ludwigsburg	2,30	0,50	1,80

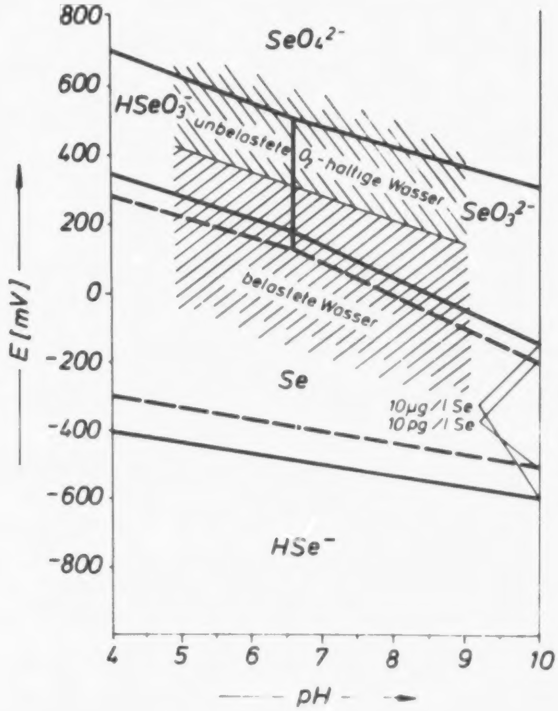


Fig. 1
Stability regions for
Se species.

unbelastete O_2haltige Wässer =
non-loaded waters containing O_2;

belastete Wässer = loaded waters

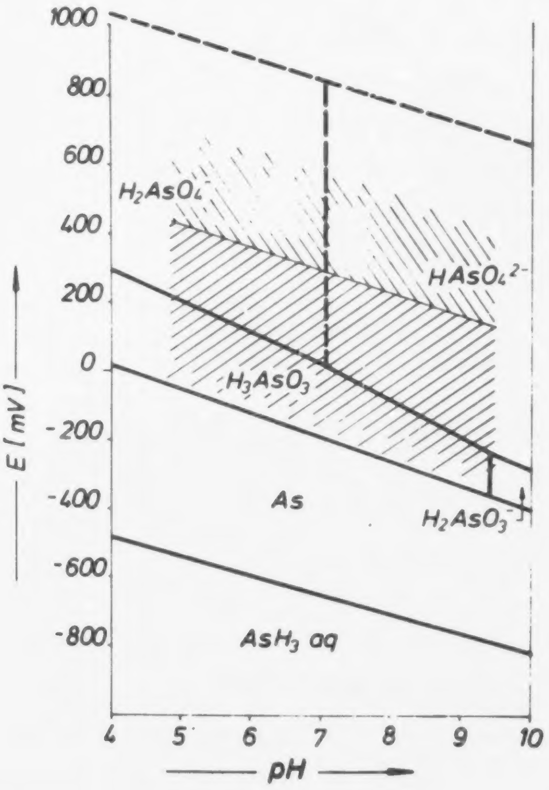


Fig. 2
Stability regions for
As species.
As ~ 10^{-6} M = 75 µg/l

More important by far for the treatment of water, however, are the reactions between chlorine and ammonia or ammonium ions. These reactions are at the basis of technologies whose application and further development are of topical significance. The technological aim is on the one hand the degradation of nitrogen by a so-called break-point chlorination in which elementary nitrogen is formed as the main product; organic nitrogen compounds are also partly involved in these processes. In the second place the formation of monochloroamine is intentionally brought about, to maintain a long-term germicidal action in extensive water-distribution systems. Chloramine is also preferred when certain substances in the water, such as phenol (1), form with the chlorine substances having undesirable odours and tastes (chlorophenols). The formation of these is substantially retarded by the presence of ammonia in the water, owing to the latter's fast reaction with chlorine.

When chlorine is added to water, hypochlorous acid is produced by hydrolysis, which dissociates to the hypochlorite ion according to the pH and the buffer capacity of the water. If ammonia is present, mono-, di-, and trichloroamine are then formed:

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$

Monochloroamine is produced first in a second-order reaction (2), i.e. in dependence on the concentrations of both reaction partners. On the basis of kinetic investigations a molecular mechanism is assumed for this reaction, i.e. the reaction is dependent on the pH and hence on the dissociation equilibria of ammonia and hypochlorous acid. In contrast to the case of monochloroamine formation, the rate constant for the chlorination to dichloroamine as a non-catalysed reaction of second order is lower by a factor of 10^4, because NH_2Cl is less nucleophilic in comparison with NH_3.

In various studies it was further established that the formation of dichloroamine is associated with acid catalysis via the pH and that disproportionation of monochloroamine also plays a part in this reaction. In addition to direct chlorination of the monochloroamine at the nitrogen by a second molecule:

$$2NH_2Cl \rightleftharpoons NH_3 + NHCl_2$$

another two-stage mechanism can also take place:

$$NH_2Cl + H_2O \rightleftharpoons NH_3 + HOCl$$
$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$

This comprises a slow first-order hydrolysis followed by a fast formation of dichloroamine. Any ammonia or ammonium present competes with the monochloroamine and exerts a stabilizing effect both on the monochloroamine and the dichloroamine.

Little information is available on the kinetics of the trichloroamine formation, but it may be assumed that the uncatalysed chlorination proceeds very slowly to the third stage. The optimal pH is below 4; at higher pH the chlorine must be used in excess. To illustrate the course of the reactions of chlorine with ammonia, knowledge of which is of considerable interest to the treatment of drinking water, universal break-point diagrams were constructed in three-dimensional representation (3) (Fig. 3). The formation and degradation of chloroamines in dependence on the chlorine addition can be

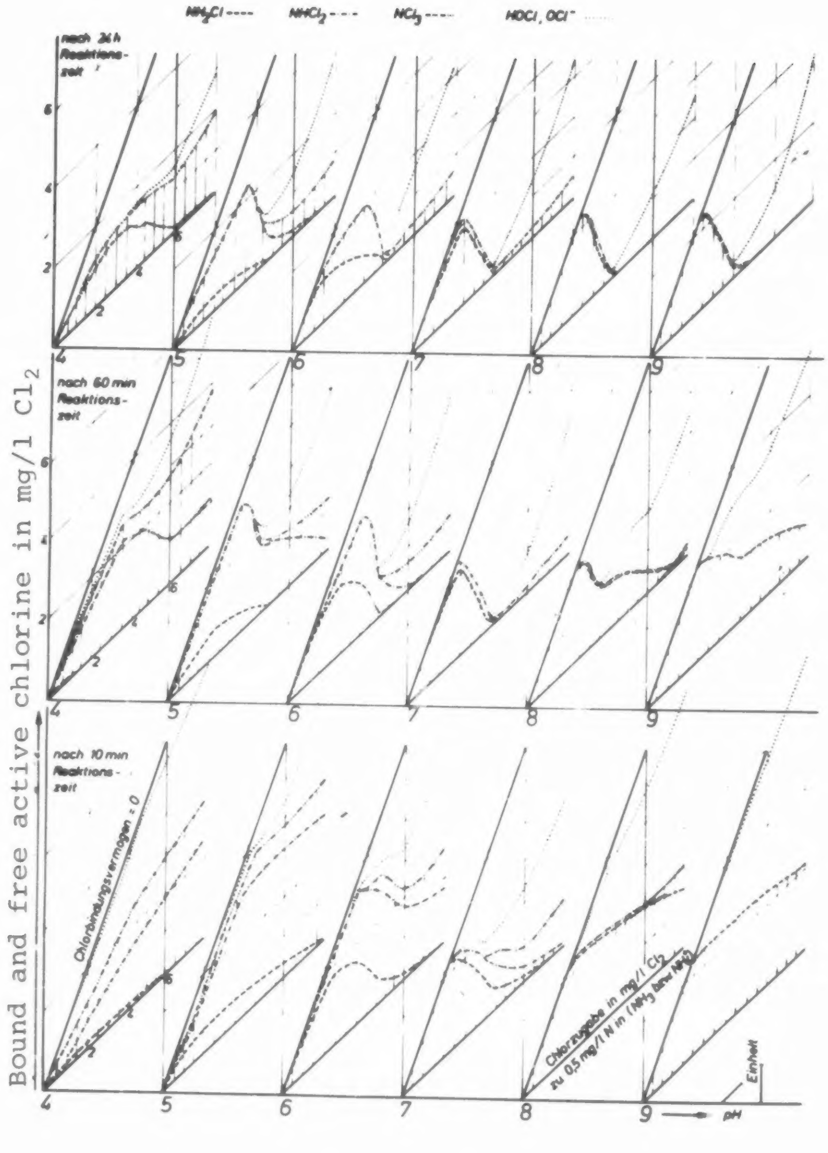


Fig. 3 Universal break-point diagrams

nach ... Reaktionszeit = after ... of reaction time;
Chlorbindungsvermögen = chlorine-binding capacity;
Chlorzugabe in mg/l... = chlorine addition in mg/l Cl_2 to 0.5 mg/l N in (NH_3 or NH_4^+);
Einheit = unit;

seen from the diagrams; the break-point formation after various action times at pH 4 - 9 is shown in addition. The stability regions for hypochlorous acid and hypochlorite and for the individual chloroamines can be represented, as for selenium and arsenic (3,4) (Fig. 4).

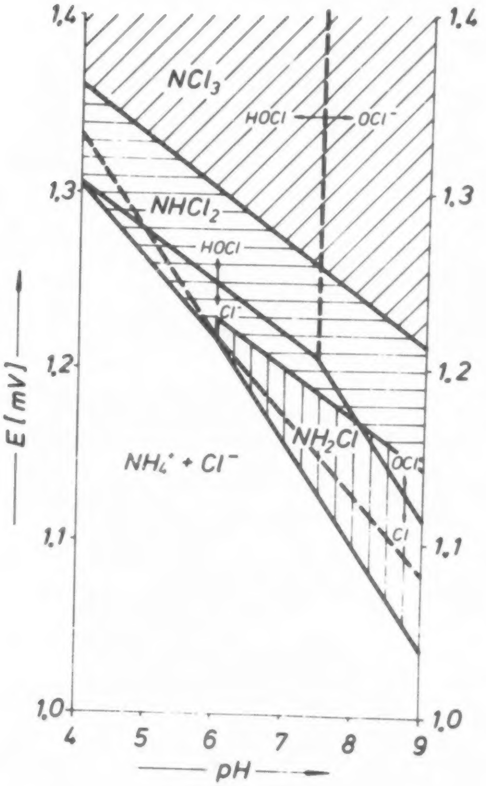


Fig. 4
Stability regions for HOCl/OCl^-
and chloroamines;
Concentration range
5 x 10^{-6} M~0.36 mg/l Cl_2

Following the addition of chlorine to a water containing ammonia or ammonium ions (or the other way round), the following pattern is observed: at a pH of about 7 and higher monochloroamine is formed; below this pH the formation of dichloroamine and trichloroamine is preferred.

Break-point formation is also impaired, because the excess of HOCl contributes to a stabilization of trichloroamine; the presence of trichloroamine in water is undesirable on account of its irritating action. The monochloroamine-dichloroamine ratio is determined mainly by the pH and less by the excess of ammonia. However, an excess of ammonia slows down the degradation of mono- and dichloroamine.

The degradation reactions of the nitrogen compounds proceed most rapidly in the region of pH 7. Monochloroamine, which is relatively stable in the presence of ammonia, is degraded by an excess of chlorine:

$$2\ NH_2Cl + HOCl \longrightarrow N_2 + H_2O + 3\ H^+ + 3\ Cl^-$$

However, this over-all equation does not provide any insight into the mechanism. It has been found (5) that the break-point formation is essentially influenced by the intermediate occurrence of dichloroamine, which is in turn decomposed via nitroxyl radicals with an increase of free chlorine to nitrogen as the main product (partly also to nitrate).

$$2\ NHCl_2 + H_2O \longrightarrow N_2 + 3\ H^+ + 3\ Cl^- + HOCl$$

The chlorine-nitrogen ratio is most favourable in the region of pH 7; at 0.5 mg/l N as NH_3 or NH_4^+ in the water this ratio is 8.2:1 by weight or 1.64 moles per mole. This ratio changes slightly to the chlorine side at higher pH but strongly at lower pH, i.e. more chlorine is used up; moreover, a lower pH is also undesirable because the desired break-point formation is then not attained; only a partial degradation of nitrogen compounds occurs. The nitrogen remains in the water for a longer time, largely as dichloroamine and trichloroamine.

Since most natural waters have a neutral pH, reactions of this kind are not immediately expected. However, during water treatment, the situation can change. Relatively small shifts of pH in the course of the treatment, e.g. due to loss of CO_2 as a result of a low and concentration-determined buffer capacity of the HCO_3^-/CO_3^{2-} system, affect the formation and degradation of chloroamines and thus the breakpoint development. The temperature of the water is also among such effects, because these reactions proceed more slowly at lower temperatures. However, a concentration shift also occurs in the chlorine-nitrogen compounds formed. The amount of chlorine for the oxidation of ammonia becomes somewhat smaller; also, an increase in ammonia (e.g. from 1 to 1.5 mg/l N) leads to a lower relative chlorine consumption for the oxidation; the reason for this lies in an intensified nitrate formation at lower ammonia concentrations in the water (5).

All this indicates that, like other oxidizing water treatments, chlorination can exert certain effects on the inorganic water constituents, effects that must be investigated in greater detail in the light of present-day water loadings and the legal specifications. The principles of chloroamine formation, which is both an essential reaction of chlorine with ammonia and an important water-treatment process, should also be established. Since it is precisely here that we find that the course of the reaction can differ according to the type of the water, appropriate preliminary studies on the practical performance of the process must be carried out in each individual case.

(1) BURTSCHELL, R.M., ROSEN, A.A., MIDDLETON, F.M., ETTINGER, M.B.
Chlorine derivatives of phenol causing taste and odor
J. AWWA 51 (1959), 2, 205-214

(2) MORRIS, J.C.
Kinetics of reactions between aqueous chlorine and nitrogen compounds. Principles and applications of water chemistry
Proceedings of the fourth Rudolfs Research Conference
John Wiley & Sons Inc., New York/London/Sydney (1967)

(3) WEIL, D., QUENTIN, K.-E.
Bildung und Wirkungsweise der Chloramine bei der Trinkwasseraufbereitung
Z. f. Wasser- und Abwasser-Forschung 8 (1975), 1, 5-16

(4) POURBAIX, M.
Atlas of electrochemical equilibria in aqueous solutions
Pergamon Press, London (1966)

(5) WEI, I.W., MORRIS, J.C.
Dynamics of breakpoint chlorination
Chemistry of Water Supply, Treatment and Distribution, Ann Arbor Science Publishers Inc., Michigan (1974)

CHLORINATION - PRACTICAL REQUIREMENTS FOR ITS APPLICATION

Y. Richard

Introduction

The main reason why chlorine is used in the treatment of drinking water is to allow adequate disinfection. Originally, this disinfection was carried out at the end of the treatment line, just before pumping of the water into the distribution network.

It is the aim of this report to examine not disinfection proper but the phenomena that occur in disinfection when, chlorine is introduced into the water, and during the contact time corresponding to passage of the water through the distribution network.

On the other hand, only the case of chlorine will be considered, the other oxidizing agents having been studied elsewhere, though the possible interference of these different oxidants will be alluded to.

Once the water has entered the network, there is theoretically no further chance for the pathogenic bacteria eliminated in the disinfection treatment to develop. Nevertheless, experience shows that there is a risk of contamination in various parts of the network, namely in pipe couplings, valves, and reservoirs.

The disinfectant will therefore need to reduce the risk of possible contamination, and the application method will either have to lead to an effect of persistent disinfection, or cause a residual amount of disinfectant to be maintained in the network. It is the latter requirement that is applied in chlorination.

We shall therefore try to determine the conditions of the use of chlorine allowing a residual amount of chlorine to be maintained in the distribution network. The concentration of the residual chlorine should furthermore be as constant as possible, so that it can be the same whatever the consumption situation in the distribution network.

I. Determination of the chlorine demand of a water

Two tests are needed to obtain an idea of the chlorine demand of a water. The first of these is the absorption curve of chlorine,which allows a determination of the amount needed to obtain a residue of free active chlorine (critical point); the second is a behaviour test allowing a determination of the evolution of the chlorine as a function of time.

I.1 Absorption curve of chlorine

Since this problem has already been dealt with elsewhere,we shall simply point out in Fig. 1 the various parts of the curve allowing different principles of application. It should be remembered that this curve, which gives the concentration of residual chlorine as a function of the amount of chlorine introduced, is plotted for a constant contact time. This contact time is generally made equal to the time of transit through the treatment installation.

Point A corresponds to the appearance of the residual chlorine in the water. The residual chlorine is then in the form of chloramine, and treatment at this dose will be characterized by:

- persistence of ammonia,
- no improvement in clarification (decantation, filtration) if the treatment is applied at the head of the treatment line,

- slight intensification of unpleasant taste,
- slow action on microorganisms,
- no formation of haloform compounds.

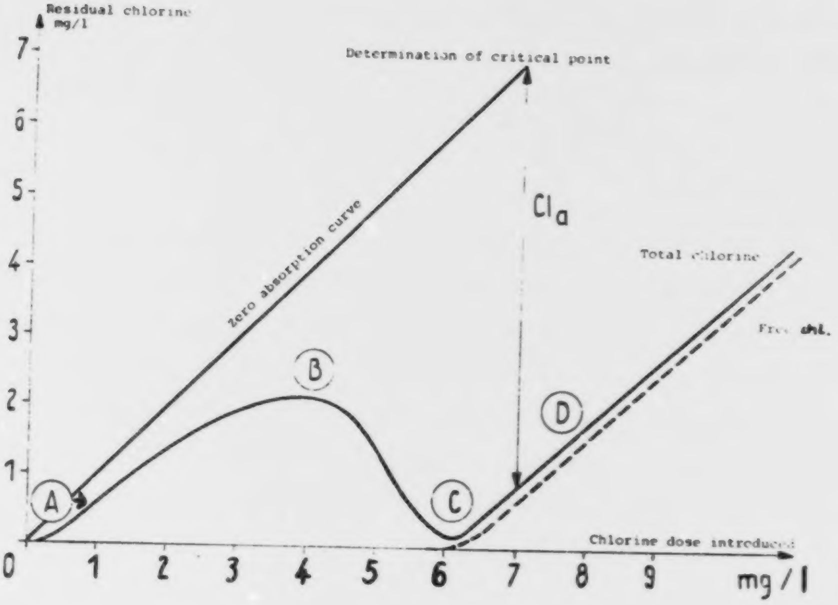


Fig. 1 Chlorine absorption curve

Point C represents the critical point; it corresponds to the appearance of free chlorine, and a prechlorination treatment at this dose will have the following effects:

- elimination of the ammonia,
- improvement of unpleasant taste,
- considerable improvement of clarification,

- effective and rapid action on microorganisms (phytoplankton and zooplankton),
- formation of haloforms.

Treatment in zone B will lead to the formation of chloramine-type compounds, with absence of free chlorine and the appearance of haloforms, while treatment in zone D will be characterized by the presence of a considerable amount of free chlorine.

I.2 Behaviour test

The behaviour test consists of introducing a certain amount of chlorine into the water, and following the residual concentration of chlorine as a function of time. One then plots against time either the concentration of residual chlorine or the amount of absorbed chlorine. The resulting curve illustrates the kinetics of the reaction of chlorine with the compounds present in the raw water. It represents the variation of the value of Cl_a, shown in Fig. 1, as a function of time.

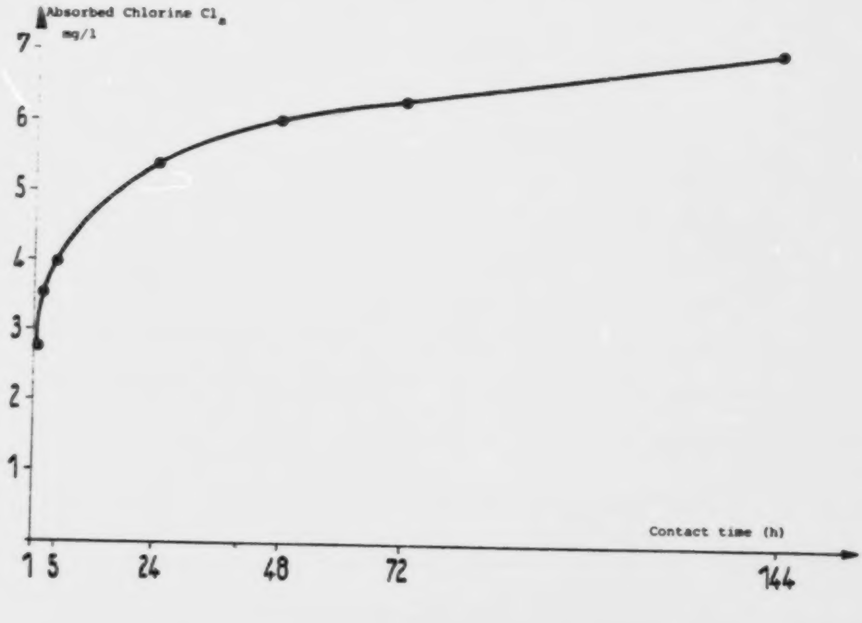


Fig. 2 Behaviour test: raw Seine water

By way of example, Fig. 2 shows the behaviour test carried out on a raw water. It was ascertained that the amount of chlorine absorbed after 2 h of contact (time of the passage through the installation) is 3.5 mg/l. After a contact time of 24 h the amount of chlorine absorbed increases to 5.3 mg/l, and after 144 h to 7.0 mg/l. A raw water directed into a network therefore consumes a large quantity of chlorine.

I.3 Consequences

It is therefore necessary to find a solution that will allow the production of a water that is as stable as possible, whose behaviour test gives the flattest possible curve, thereby indicating slight absorption of chlorine.

The first technique used was to situate the first part of the curve, where the chlorine consumption is both fastest and greatest, as early as possible in the treatment line.

This is the so-called "prechlorination" technique, in which the chlorine is introduced at entry into the treatment installation. Under these conditions the chlorine reacts more or less rapidly with all the substances dissolved or suspended in the raw water and with the reagents used during the treatment.

Prechlorination also has the advantage of a considerable improvement in the processes of coagulation, decantation,and even filtration.

Incidentally, we do not intend to consider here the technique of prechlorination with a contact time of over 24 h, which can be used when the raw water is to be stored.

In the above case, it need only be indicated that this technique can result both in certain advantages (reduction in the treatment concentration of the coagulant) and in serious disadvantages, favouring the conditions for the formation of chlorine compounds (e.g. haloforms).

II. Factors influencing the absorption curve of chlorine

These factors can be due to the water itself or to the practical conditions of application of the chlorine.

II.1 Composition of the water

The reaction of chlorine with the inorganic substances present in the water has been studied elsewhere. It is necessary to consider the possible reactions with the organic constituents of the water.

II.1.1 Nitrogen compounds and the TOC

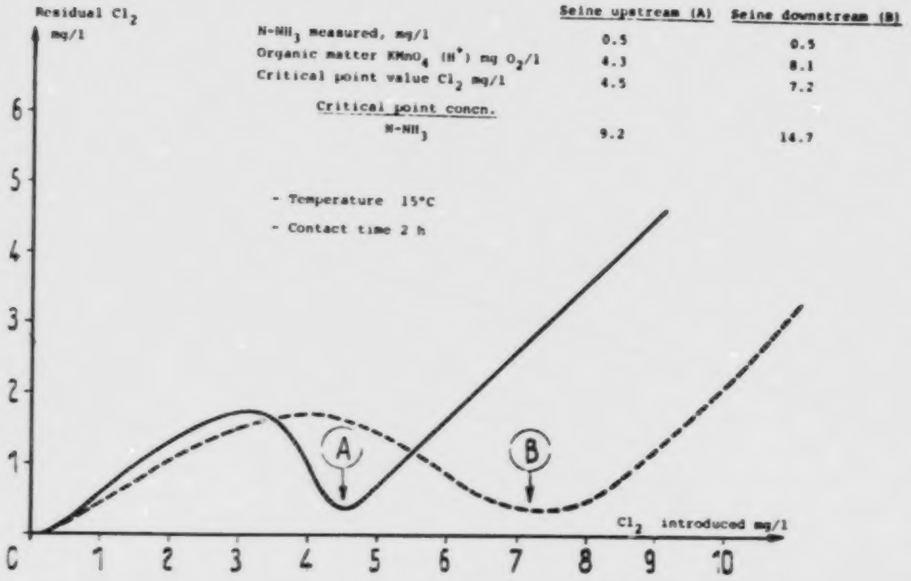
It is found that for one part of ammoniacal nitrogen it is necessary to add 7.6 parts of chlorine in order to obtain chlorination at the critical point. However, these proportions are not constant. Thus, while they apply to waters containing ammonia and only a small amount of organic matter, the ratio can rise to 15 for organically polluted water. Fig. 3 gives two examples for Seine waters containing 0.6 mg/l of NH_3, one of these coming from upstream of Paris (permanganate oxidizability measured in an acid medium 4.3 mg/l), the other from downstream of Paris (permanganate oxidizability 8.1 mg/l).

It would obviously be ideal to find a formula allowing a calculation of the critical point as a function of the concentrations of various elements X, Y, and Z present in the water of the form:

Treatment concentration for the critical point

$$= xf\,[X] + yf\,[Y] + zf\,[Z] + \ldots$$

Various examples demonstrate the difficulty of finding such a formula.



	Seine upstream (A)	Seine downstream (B)
N-NH_3 measured, mg/l	0.5	0.5
Organic matter $KMnO_4$ (H^+) mg O_2/l	4.3	8.1
Critical point value Cl_2 mg/l	4.5	7.2
$\frac{\text{Critical point concn.}}{\text{N-}NH_3}$	9.2	14.7

Fig. 3 Chlorine absorption curve

a) Example of glutamic acid

Glutamic acid is an amino acid with the following formula:

$COOH-CHNH_2-(CH_2)_2-COOH$,

containing 5 atoms of carbon, which gives a TOC value of 60 g per mole.

Its molecular weight is 147. In addition, one mole contains 14 g of nitrogen, i.e. for 1 g of nitrogen there are 4.26 g of total organic carbon, this corresponding to 10.5 g of glutamic acid.

Incidentally, glutamic acid does not correspond to the amount of ammonia in water, at the very most a very slow hydrolysis being observed. Fig. 4 shows the amount of

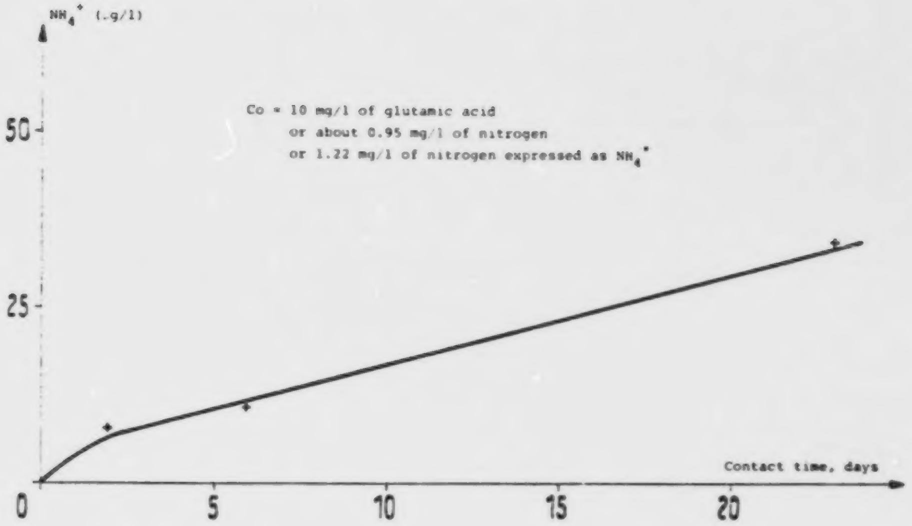


Fig. 4 Hydrolysis of glumatic acid as a function of time

nitrogen responding to an ammonia nitrogen determination as a function of time.

The formula of glutamic acid leads one to expect a certain reactivity of this substance with chlorine. Fig. 5 shows several curves for the absorption of chlorine by a solution containing glutamic acid.

The dilution water was first saturated with chlorine, then dechlorinated by means of ultraviolet radiation. The absence of chlorine absorption by the dilution water was then checked. Solutions with various concentrations of glutamic acid were used. Fig. 5 shows the results of two experiments. It can be seen that the ratio between the value at the critical point and the amount of nitrogen introduced is 10.7 (as opposed to 7.6 for ammoniacal nitrogen).

In addition, the general form of the curve is flatter than that for a substance containing ammoniacal nitrogen.

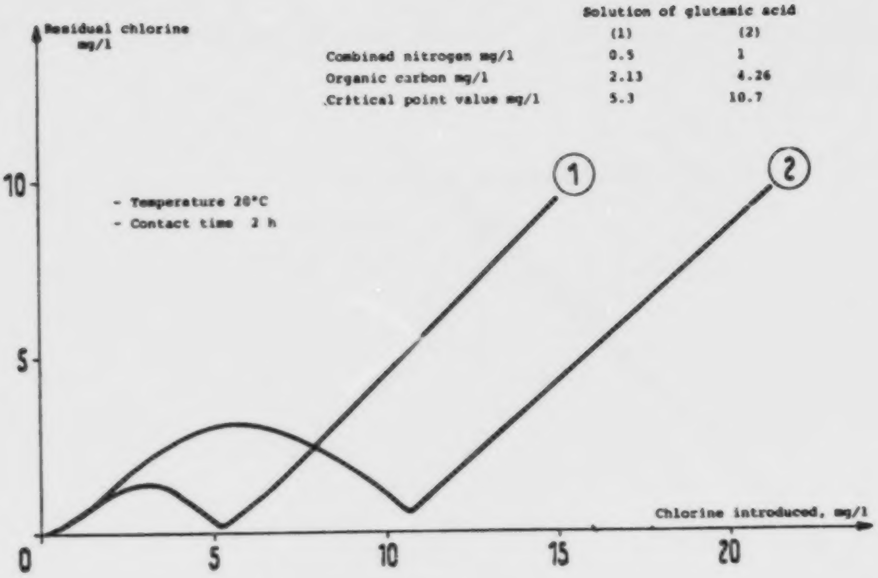


Fig. 5 Chlorine absorption curve

b) Example of amyl alcohol

This compound, $CH_3-(CH_2)_3-CH_2OH$, was chosen because it too contains 5 atoms of carbon per molecule.

The chlorine absorption curve shows negligible absorption of chlorine. One can find many examples of substances having various TOC and not giving rise to any absorption of chlorine.

c) Example of pyridine

This compound, C_6H_5N,has a high TOC and contains one nitrogen. It too does not lead to any absorption of chlorine (see Fig. 6).

d) In conclusion, it must be accepted that, while the ratio of chlorine introduced at the critical point to the nitrogen increases with increasing organic contamination of the water, it is not at present possible to link this factor with the over-all composition of the organic contamination, whatever method is used: TOC, permanganate oxidizability, UV absorption, etc.

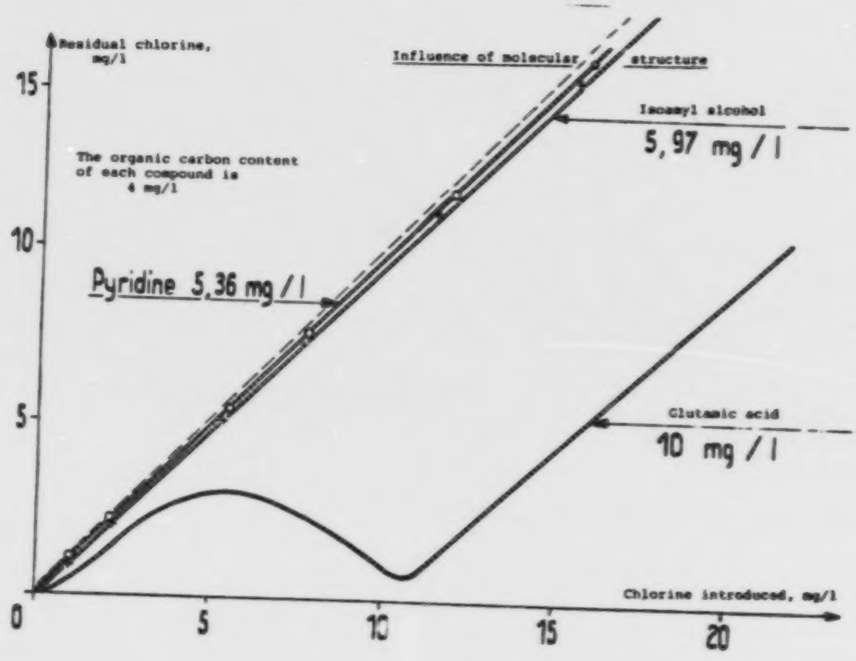


Fig. 6 Chlorine absorption curve

II.1.2 Phenols

Fig. 7 shows the results of a study into the elimination of phenol products by chlorination of a water that also had a high level of industrial pollution, the untreated mixture containing various dimethylphenols and o-cresol. Chlorination of these compounds results in the appearance of a critical point. Below the critical point the formation of chlorophenols causes an intensification of unpleasant flavour, while above the critical point addition compounds saturated with chlorine no longer correspond to the amount of phenol, and the unpleasant flavour is almost non-existent.

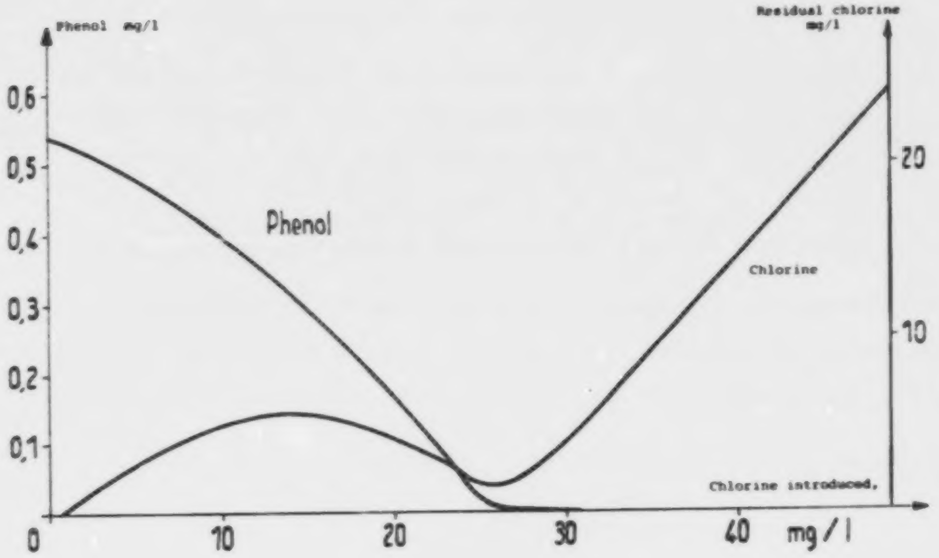


Fig. 7 Elimination of phenolic compounds by chlorination of an industrial water

Thus, phenol too participates in the absorption of chlorine in water, and chlorination at the critical point allows the organoleptic properties of water to be improved.

II.1.3 Conclusions

It would seem at present that it is not possible to determine the value of the critical point of a water from contamination analyses habitually carried out on water. At the most, one can assume that the ratio chlorine introduced at the critical point/ammoniacal nitrogen increases as a function of organic pollution, even though it is not possible to pinpoint this value within the range between 7.6 and 15.

II.2 Variation of the chlorine absorption curve

Several factors may cause the absorption curve of chlorine in water to vary. Some of these may increase the chlorine demand of a water, while others may mask it.

II.2.1 Increase of the absorption of chlorine by water

This concerns all reagents that may cause a supplementary absorption of chlorine. A typical case is the use of silica activated with ammonium sulphate. Fig. 8 shows its effect:

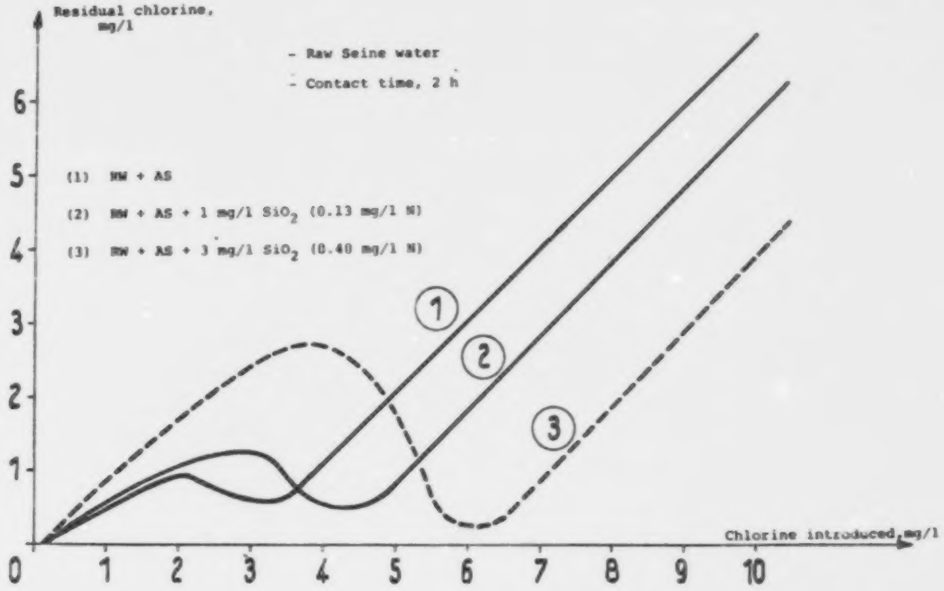


Fig. 8 Effect of the use of silica activated with ammonium sulphate

for treatment concentrations of activated silica (SiO_2) of between 1 and 3 mg/l, i.e. for amounts of nitrogen (expressed as N) introduced into the water equal respectively to 0.13 and 0.40 mg/l, one observes an increase in the value of the critical point, which rises from 3.2 to 4.2 and 6.2 mg/l of chlorine. At the same time, the form of the absorption curve changes, tending towards the typical form obtained with a pure solution of ammoniacal nitrogen.

II.2.2 Effect of powdered activated carbon

In the face of the degradation of the organoleptic properties of raw water, activated carbon has been used more and more often. The powdered form is now used most frequently, at least at the start, when the use of the activated carbon may be periodic. The carbon is introduced during coagulation-flocculation, in order to profit from the time of contact required for the flocculation.

The use of powdered activated carbon in diffuse flocculation units, situated upstream of static or plate decantation units, does not involve any appreciable change in the methods of application of prechlorination.

In contrast, in the case of sludge-bed decantation units (Accélator or Pulsator types), some changes in the observed phenomena do occur.

Thus, the use of a treatment concentration of 15 mg/l of powdered activated carbon allows a concentration effect to be obtained in the sludge bed, where the concentration of activated carbon can reach 1 g/l. This has a favourable effect on adsorption, and it is important to determine more precisely the effect on prechlorination.

Fig. 9 shows chlorine absorption curves obtained in an installation with and without activated carbon.

A very flat curve is found in the case of the treatment using powdered activated carbon, which is advantageous for operation: a sudden variation of the critical point will not disturb the residual concentration of chlorine in the treated water. It is important, on the other hand, to determine its effect on the treatment of the water itself. To this end, the installation, which included a Pulsator decantation unit,

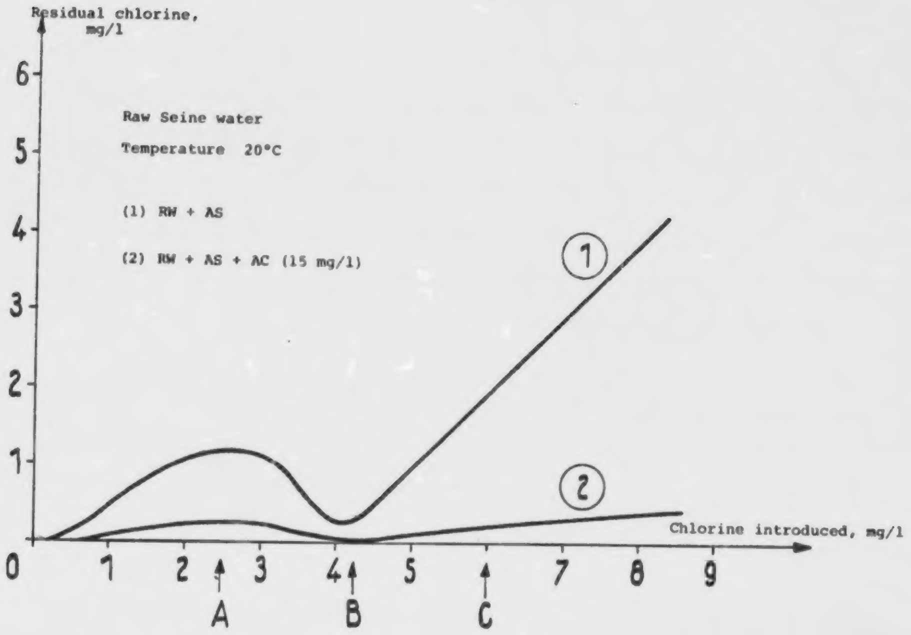


Fig. 9 Absorption of chlorine with or without powdered activated carbon

was operated with prechlorination treatments at points A (2.5 mg/l, i.e. below the critical point), B (4.25 mg/l, at the critical point itself), and C (6 mg/l, i.e. above the critical point).

The water, industrially filtered through sand, was sampled after each of these treatments, and the chlorine absorption curve was plotted for each sample.

The results (Fig. 10), lead to the following observations:

- in water C there is no secondary consumption of chlorine,
- in water B the absorption curve develops normally without any significant secondary consumption,

in water A, a secondary absorption of chlorine and the appearance of a critical point at a treatment concentration of 1.8 mg/l are observed. If one adds together the treatment concentration and the concentration used previously during decantation with powdered activated carbon (2.5 mg/l), one obtains a total of 4.3 mg/l, while the treatment concentration without activated carbon is 4.1 mg/l.

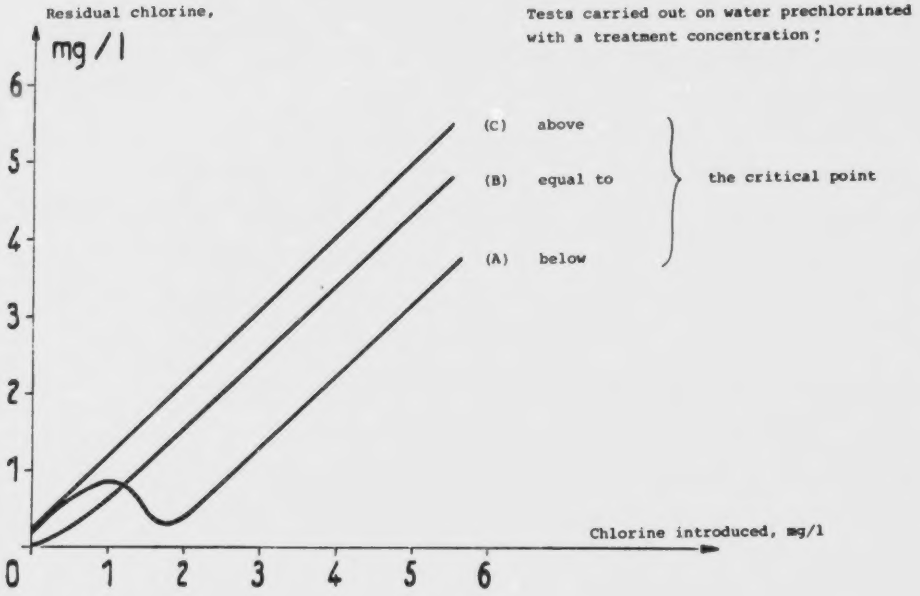


Fig. 10 Chlorine absorption curve for a water treated with powdered activated carbon

The excess chlorine absorption is thus only 0.2 mg/l for the installation under consideration, the introduction of activated carbon being carried out 30 sec after the introduction of the chlorine, for the same quality of raw water.

The use of powdered activated carbon under these conditions has hardly any effect on the prechlorination treatment, apart from a very slight excess absorption.

Incidentally, recent studies have shown that it was futile, from the bacteriological point of view, to provide a raw water-chlorine contact time of the order of 15 min before the introduction of the powdered carbon.

Prechlorination can therefore be carried out without any drawbacks, in a decantation unit using powdered active carbon, the carbon not impeding the oxidizing action of chlorine on products that contain nitrogen in the form of ammonia, but allowing the adsorption of certain precursors of the formation of haloforms.

III. Factors influencing the behaviour of the test

In certain cases the chlorine demand of water varies without the chlorine absorption curve showing a proper critical point. The action of ozone interferes with the chlorine, and it has proved possible to demonstrate a relationship between the humic acid index and the chlorine demand of a water.

Numerous tests have been carried out on this interference, which can be summarized in the following experiment.

Raw river water is subjected to the following treatment:

- prechlorination with a dose higher than the critical point (or break-point),
- coagulation-flocculation-decantation,
- adsorption treatment with powdered activated carbon added to the decantation unit,
- filtration.

This produces a treated water of excellent quality, whose characteristics are as follows:

- pH : 7.4
- Colour (mg/l of Pt Co) : 5
- Suspended matter (mg/l) : 0.3
- Turbidity (JU) : 0.1
- $KMnO_4$ oxidizability (acid medium, mg O_2/l) : 1.25
- CAT (°F) : 16
- HT (°F) : 25
- Anionic detergents (mg/l) : 0.10
- Phenols : not detected

This treated water (water T) was subjected to a chlorine absorption test as a function of time, the results of which are given in Fig. 11.

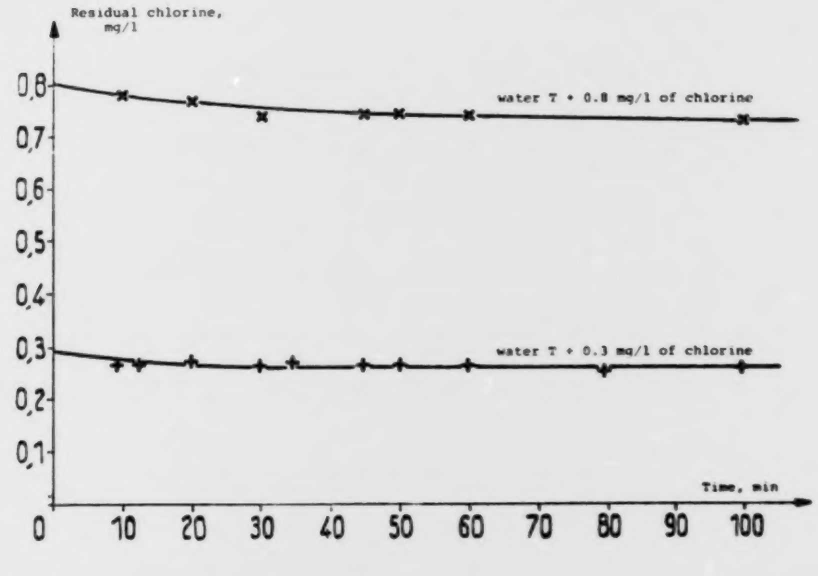


Fig. 11 Chlorine absorption curve for water T as a function of time

It can be seen that the water absorbs practically no more chlorine, which would seem obvious a priori, since the water was previously treated with a treatment concentration higher than the critical point value. This applies to the two treatment concentrations tried: 0.3 mg/l and 0.8 mg/l, and the chlorine absorbed in 100 min was respectively 0.03 and 0.06 mg/l, which is of the order of the experimental error.

Fig. 12 shows the same water T treated again with 0.3 mg/l of chlorine to check the absorption of chlorine in this sample; the absorption is virtually non-existent.

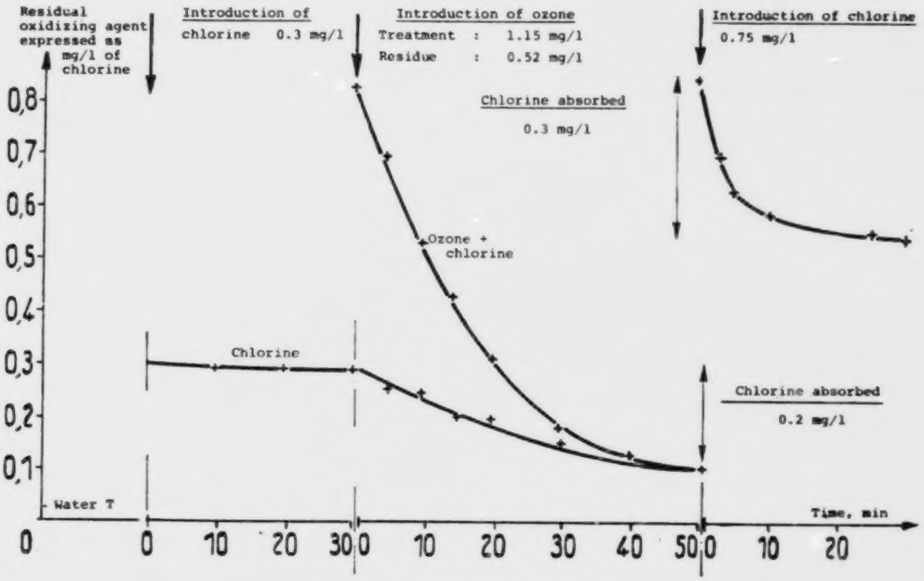


Fig. 12 Effect of ozonization on the absorption of chlorine

Ozonization of the water was carried out after 30 min of contact. The treatment concentration was 0.8 mg/l (or 1.15 mg if this dose is expressed as a chlorine equivalent, as on the graph) which ensures an ozone residue of 0.35 mg/l (or 0.52 expressed as the chlorine equivalent). The total contact time in two contact columns was 8 min: 4 min plus 4 min.

The water was then left to stand and the total residual oxidizing agent and the total residual chlorine were measured. The difference between the resulting curves represents the evolution of the residual ozone, expressed as chlorine. A reduction in the amount of residual ozone is found, which is normal, but there is also a reduction in the residual chlorine: consumption of chlorine does, therefore, take place, in this case in an amount of 0.2 mg/l after 50 min of contact. To confirm this finding, a new chlorine absorption test was carried out: 0.75 mg/l of chlorine was introduced into the water, and the residual chlorine was checked as a function of time: a sudden fall in the residual chlorine was found: 0.25 mg/l was absorbed in 10 min and 0.30 mg/l in 30 min.

In all, the ozone treatment thus caused a secondary consumption of chlorine, amounting to 0.5 mg/l in the case in question.

In an attempt to define more accurately this secondary absorption of chlorine, trials were carried out in another installation treating a Loire water. Fig.13 shows the variation of the chlorine demand of this water as a function of time for up to 24 h of contact. The demand varies according to the stage of the treatment, and we have compared it to the amount of humic acid present. Fig. 14 shows the relationship obtained between these two factors.

It can be seen that the reduction in the amount of humic substances allows the chlorine demand of a water to be considerably reduced. This elimination will at the same time reduce the quantity of certain haloform precursors during chlorination.

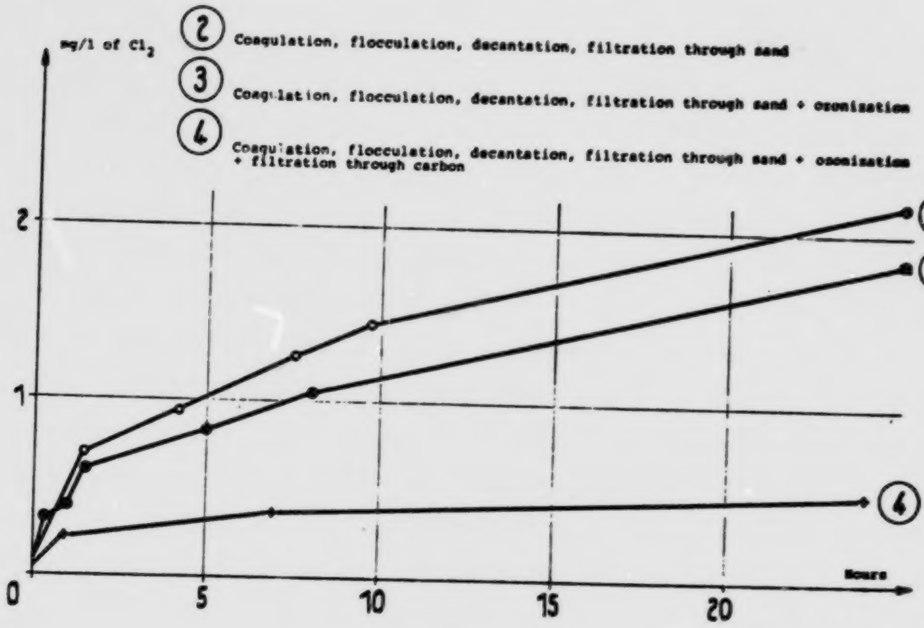


Fig. 13 Chlorine demand of waters

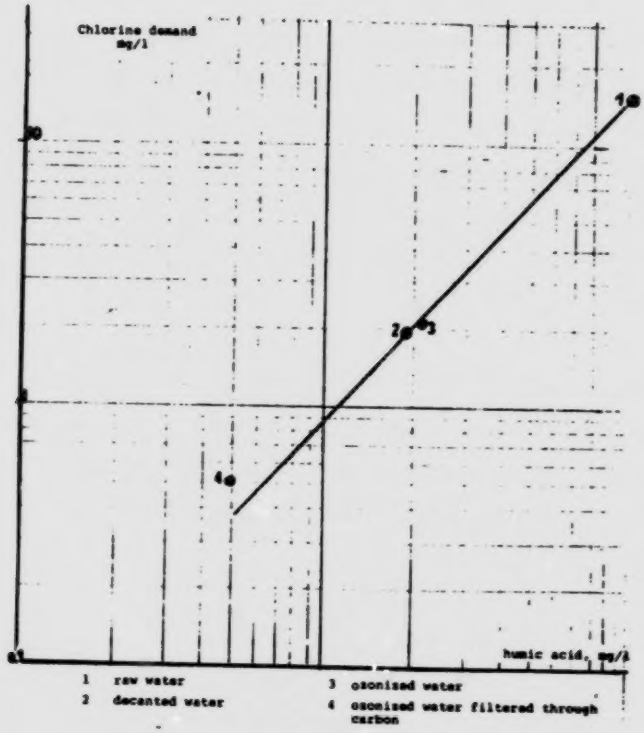


Fig. 14 Effect of the humic acid concentration on the chlorine demand of water

IV. Conclusion

Taken together, these observations allow a determination of the procedure to follow in the application of a chlorination technique:

- Avoid chlorination in conjunction with prolonged storage of raw water.
- As far as possible, eliminate organic and humic material by regulating the clarification treatment more precisely. In particular, it will be necessary to adjust suitably the treatment concentration of the coagulant, for the sake of a better elimination of colloids and organic matter, and to avoid insufficient treatment by seeking an acceptable turbidity while allowing organic matter capable of being eliminated at this stage to remain.
- It is possible to use a small dose of powdered activated carbon at the coagulation-flocculation-decantation stage. The sludge-circulation or sludge-bed decantation units favour this effect.
- In the case of prechlorination, treat at the critical point, but avoid treatment too far above it.
- Again in the case of prechlorination, adopt sufficiently high rates of decantation and filtration to avoid conditions favouring the formation of haloforms.

In all these cases a complete and well applied treatment, as regards both clarification and adsorption on granulated activated carbon, should allow the potential of chlorination to be utilized as far as possible, while avoiding the adverse effects that chlorination can provoke if it is incorrectly carried out.

CHARACTERIZATION OF ORGANIC WATER CONSTITUENTS BY THE KINETICS OF CHLORINE CONSUMPTION

H. Bernhardt and O. Hoyer

1. Introduction

With increasing eutrophication of the Wahnbach dam in recent years the chlorine demand for the disinfection of treated drinking water increased as well. Only with the aid of repeated post-chlorination in the distribution network could it be ensured that the water in the towns and communities supplied still contained some chlorine. In spite of this increase in post-chlorination, in recent years sudden bacterial growth has been occurring more and more often in some parts of the pipelines and overhead tanks. This growth pointed to a reduced safety of the drinking water supply and was the reason why we started a detailed study into the extent and the course of the chlorine consumption in water. In the course of this work we discovered that the dam water consumes different amounts of chlorine at different times of the year. Fig. 1 shows that the chlorine consumption of the dam-water to be treated is essentially lower during winter than during the summer, when intensive growth of algae takes place and algal organic compounds are released into the water. These changes in the quality of the dam water, however, cannot be detected by determining the content of dissolved organic compounds (DOC), since the concentration change of the DOC is relatively small.

Detailed investigations, carried out because it had been shown that the flocculation process in the treatment of the dam water with aluminium salts is affected by the composition of the biogenic organic substances in the water, have demonstrated the influence of algal substances on water treatment (1).

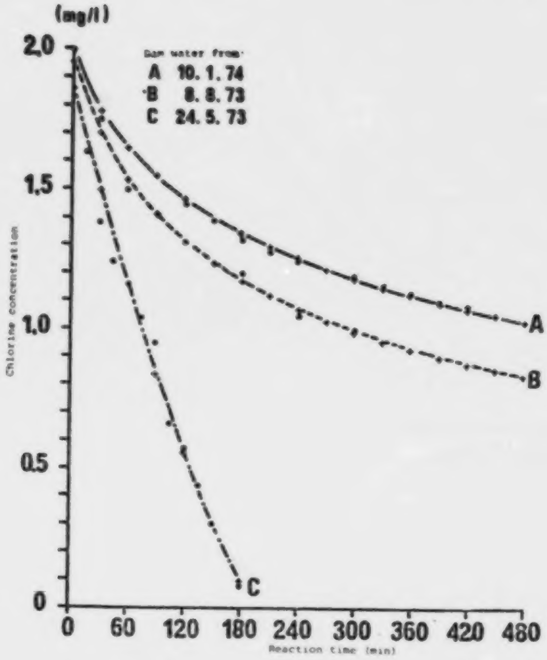


Fig. 1

Chlorine consumption curves for dam water at various times of the year

Determination of the chlorine consumption as an analytical procedure for characterizing water with respect to its organic substance content has been performed for years, but has lost ground in recent years. A report on the various procedures used for the determination of the chlorine consumption of water will be found in an earlier paper (2). Since the latter work also contained a detailed bibliography, this will be omitted here.

2. Investigations of chlorination kinetics

If a certain amount of chlorine is added to a water sample and the fall of the chlorine concentration is followed continually as a function of time, statements can be made about the kinetics of the chlorine consumption. For this purpose it is useful to plot the logarithm of the chlorine concentration measured in the sample against time. Fig. 2 shows the course of the chlorine consumption for two different

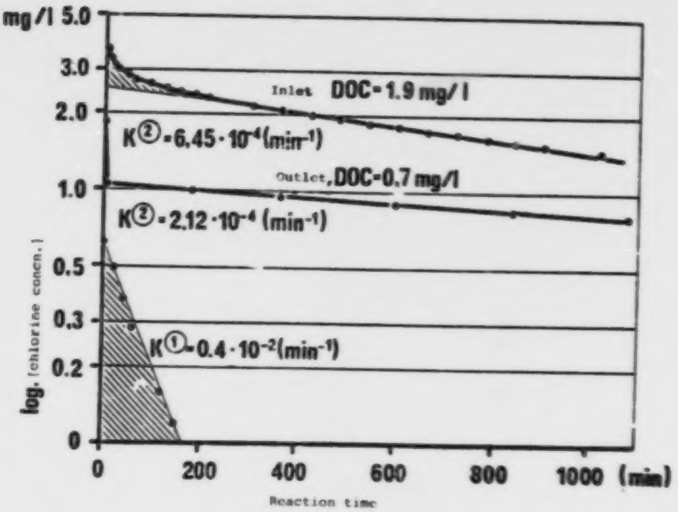


Fig. 2 Chlorine consumption in water samples from the Wahnbach auxiliary dam (inlet) and from the filtrate of the P-elimination plant (outlet) (27 July 1978)

waters in such semi-logarithmic representation. One of the samples was water from the Wahnbach auxiliary dam, considered as strongly eutrophic, and the other the filtrate from a phosphorus-elimination plant by the Wahnbach dam, in which the content of organic substances is diminished by 50 - 70% by the treatment step, depending on which parameters are used to evaluate the organic substances. From these curves, which are reproduced schematically in Fig. 3, it can be seen that the chlorine consumption can be resolved into:

a) a spontaneous consumption that takes place extremely rapidly and cannot be followed as a function of time with our measuring procedures,

b) a rapid chlorine consumption within the first 3 h (in the shaded region) and

c) a slowly progressing chlorine consumption, which can be observed over the subsequent longer period of time.

$$C(t) = C^{①}(t) + C^{②}_{(t)} = C_0^{①} \cdot e^{-K^{①} \cdot t} + C_0^{②} \cdot e^{-K^{②} \cdot t}$$

$$C^{\Delta}(t) = C(t) - C_{(1000\,\mathrm{min})} = C_0^{\Delta} \cdot e^{-K^{\Delta} \cdot t} \quad \text{for } 120\,\mathrm{min} \leq t \leq 600\,\mathrm{min}$$

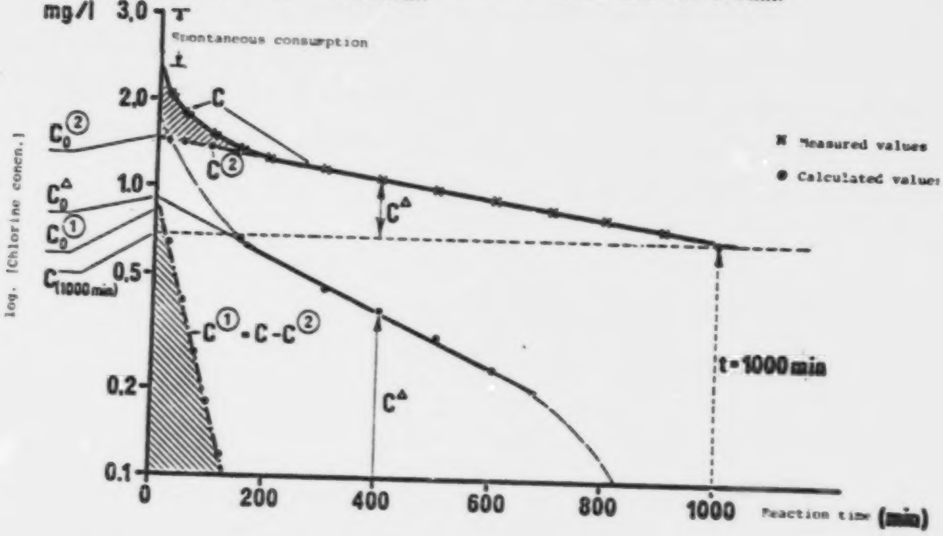


Fig. 3 Diagram for the calculation of magnitudes from the course of the Cl_2-concentration against reaction time. The spontaneous consumption is not included in the Cl_2-concentration at time t = 0

The semi-logarithmic representation shows that the slow consumption of chlorine takes place linearly with time, so that this slow consumption phase can be described by a first-order rate equation whose rate constant K^2 is calculated from:

$$K = \ln C/C_0 \cdot t^{-1} \quad (\mathrm{min}^{-1})$$

To obtain the rate constant K^1 of the fast reaction, the fraction of the chlorine concentration corresponding to the slow consumption rate is extrapolated to t = 0. By subtracting this fraction of the concentration from the total chlorine concentration present at the time, the fraction of chlorine concentration corresponding to the fast reaction is obtained. Plotted semi-logarithmically against time, this fraction of the concentration also gives a straight line, and thus also corresponds to a first-order reaction. It is remarkable that the complex chlorine-consumption reaction can be represented empirically by two superimposed first-order reactions with rate constants differing in nearly all cases by two powers of ten. As Fig. 2 shows, for the water sample from the auxiliary dam (inlet):

$$K^1 = 0.4 \cdot 10^{-2}\ (\mathrm{min}^{-1}) \quad \text{and}$$
$$K^2 = 6.45 \cdot 10^{-4}\ (\mathrm{min}^{-1}),$$

while in the case of the chlorine consumption by the filtrate from the phosphorus-elimination plant no value for K^1 was found and K^2 was only $2.12 \cdot 10^{-4}$ (min^{-1}).

The higher the rate constant measured, the faster does the chlorine consumption take place in the respective water sample. The rate of this chlorine consumption is determined solely by the nature and the amount of the organic substances present in the water. It was found that ammonium ions are not included by the rate constants K^1 and K^2. With the aid of continual measurements of the chlorine consumption and the determination of the rate constants, it is also possible to characterize a water with respect to its content of organic material. Continual measurements of the course of the chlorine consumption therefore constitute a further sum parameter for the evaluation of water, with particular reference to the chlorine-consuming organic substances.

3. Performance of the chlorine-consumption measurements

The measurement of the chlorine consumption as a function of time is carried out on 5-litre samples in brown glass bottles. This volume size eliminates the possibility of a wall-effect (cf. Maier and Mäckle) (3), which can simulate a high and unrealistic chlorine consumption. We have already reported on this point (2).

The fall in the chlorine concentration against time is measured continuously with an automatic analyzer. For this we set up the Autoanalyzer 2 (Technicon) in accordance with the German unit process G4 (DEV G4), in such a way that during a measurement over 24 h the water volume of the sample decreases by only 20% at the most. The measurement region was between 0.05 and 10 mg/l of chlorine. To be able to measure the sample with the Autoanalyzer the sample must be free from particular substances, and it is therefore necessary to filter the test sample through a membrane filter with pore diameters of 0.45 μm. The method for the determination of active and free chlorine for the Autoanalyzer input according to the DEV G 4 is described elsewhere (4).

4. Influence of the chlorine-carbon ratio on the chlorine consumption kinetics

The chlorine reaction here under discussion is a complex reaction of many organic compounds, not known individually, with only one reaction partner, chlorine. Since the different materials react with the chlorine at different rates, a sufficient amount of chlorine is necessary, so that the fast reactions are not preferred to the simultaneously occurring slow reactions. If this were allowed to happen, the fast reactions would use up the available chlorine too quickly, so that not enough chlorine would be left for the slow reactions, and the course of the over-all consumption would be falsified. Therefore, the chlorine-carbon ratio established at the outset of the kinetic measurements is of decisive importance.

Our detailed investigations were concerned with the influence of the chlorine-carbon ratio on the rate constants. For these experiments we used as typical water constituents high-molecular weight organic acids (humic acids) isolated from the water of the Wahnbach dam in April 1978. We obtained these humic acids by alamine extraction and molecular weight separation with an Amicon UM-2 membrane, exclusion limit MW 1000 (5,6). The procedure was to add a suitable amount of DOC to a 5-litre sample with a specified chlorine content. Blank consumption of chlorine could thus be eliminated.

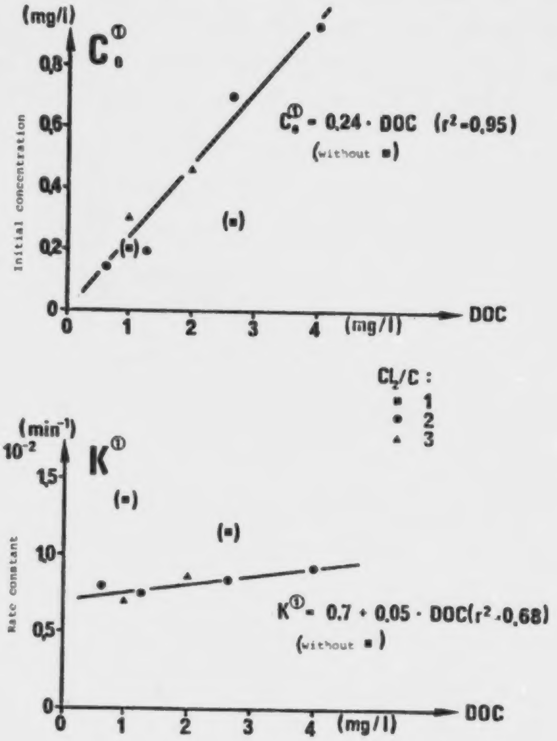


Fig. 4 Initial concentration C_o① and rate constant K_o① for the fast partial reaction ① of the chlorine consumption in dependence of the DOC with various Cl_2/C ratios

The results of these experiments have been compiled in Figs. 4 and 5. Fig. 4 shows that the rate constants of the first fast chlorine consumption (K^1) for chlorine-carbon ratios (weight concentration ratios) of 2 or 3 in the region of 1 - 4 mg DOC/l are approximately constant. With a chlorine-carbon ratio of more than 2, on the basis of the chlorine excess then present, the initial chlorine concentrations C_o^1 obtained by extrapolation (see Fig. 3) are proportional to the concentrations of dissolved organic carbon (DOC) present in the water (see the upper part of Fig. 4). This shows that above a chlorine-carbon ratio of 2 the chlorine concentration provided is sufficient for the fast chlorine-consumption reactions.

For the slow chlorine-consumption reaction the situation is not so favourable. Fig. 5 shows that rate constants are not independent of the DOC until the chlorine-carbon ratio reaches or exceeds 3, and then remain constant. At a chlorine-carbon ratio of 2 there is still a slight variation of the rate constants with the DOC. A chlorine-carbon ratio 1 means in all cases an insufficiency of chlorine. This can also be derived from the dependence of the initial chlorine concentrations C_o^2 obtained by extrapolation (cf. Fig. 3). Not until a chlorine-carbon ratio of more than 2 has been reached is the chlorine excess provided sufficient for an optimal chlorine-consumption reaction and the C_o^2 values calculated are proportional to the DOC.

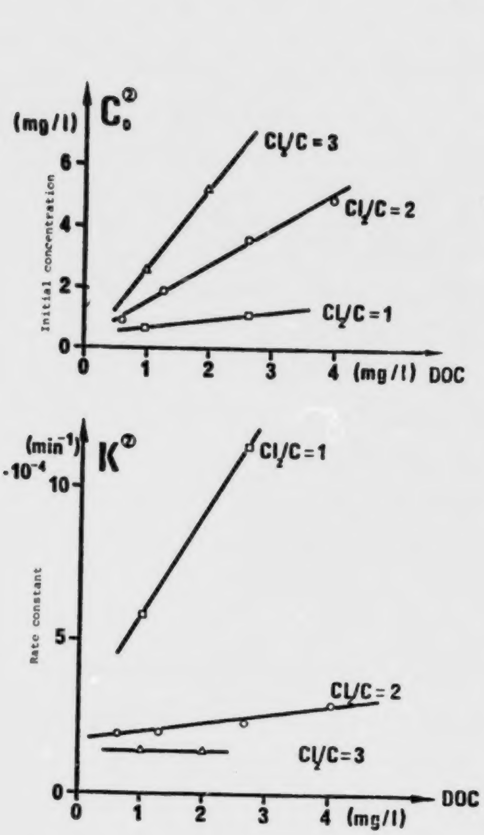


Fig. 5 Initial concentration $C_o^{②}$ and rate constant $K^{②}$ for the slow partial reaction ② of the chlorine consumption in dependence of the DOC with various Cl_2/C ratios

An attempt was also made, by forming differences, to calculate a rate constant independent of the actual chlorine concentration in the samples and thus independent of the chlorine-carbon ratio. For this purpose the chlorine concentration after 1000 min of reaction time ($C_{1000\ min}$) was subtracted from the chlorine concentration C obtained and plotted as a separate curve in semi-logarithmic coordinates in Fig. 3 (curve C). Extrapolation of the middle, linear part (125 - 600 min) of this relative chlorine consumption curve to t = 0 gives the calculated initial chlorine concentration C_o. From Fig. 6 it can be seen that for chlorine-carbon ratios of 1 to 3 the initial chlorine concentrations so obtained increase in proportion to the DOC content and independently of the chlorine-carbon ratio. Unfortunately, however, the rate constants K calculated in this way (the lower part of Fig. 6) for the DOC-concentration range of 1 - 4 mg/l are not as independent as was hoped. The scatter of the individual values for the different chlorine-carbon ratios is so unsystematic that no curve must be drawn through these points. The same unsystematic variation of the results was observed in the evaluation of the kinetic chlorine consumption experiments on different waters. These relative rate constants were therefore not introduced as a means of characterizing waters.

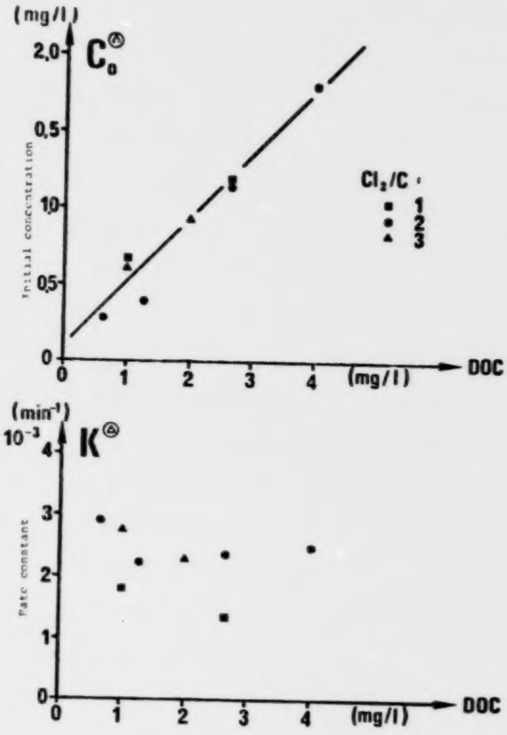


Fig. 6 Initial concentration $C_o^{\textcircled{\Delta}}$ and rate constant $K^{\textcircled{\Delta}}$ for the chlorine consumption obtained from the difference in the chlorine concentration after 1000 min of consumption in dependence on the DOC with various Cl_2/C ratios

5. Formation of organochlorine compounds during a 20 h chlorine action period

Both the high-molecular and low-molecular weight organochlorine compounds are formed in the reaction of chlorine with a mixture of organic substances in water. In this respect it is interesting to ask whether there is a connection between the chlorine consumption and the amount of organochlorine compounds formed. Therefore, at the end of a chlorine reaction time of 20 h the total content of organic chlorine compounds formed (TOCl) and the content of haloforms were calculated and related to the concentration of organic carbon compounds (DOC), with an allowance for the chlorine-carbon ratios in each case. The results obtained for our model substance (humic acid as auxiliary dam water) are collected in Fig. 7, according to which both the formation of haloforms and of the total organic chlorine (TOCl) takes place in proportion to the concentration of organic compounds in the water samples, irrespective of the selected chlorine-carbon ratio. Thus, above a certain minimum chlorine amount it does not matter for the formation of TOCl and haloforms how high the concentration of chlorine is in relation to the DOC concentration present, provided that a sufficiently long reaction time is allowed. The experiments have shown that a period of 20 h is sufficient. This finding is decisive for the practice of water treatment in respect to the chlorination and the transport times of the water to the consumer. It shows that, independently of whether the water has been subjected to preliminary chlorination, high chlorination, or break-point chlorination, increasing concentrations of organochlorine compounds in the water must be reckoned with whenever increasing concentrations of dissolved organic compounds are present in the water to be treated if the compounds are capable of reacting with chlorine (precursors). Further trials (see Fig. 12) have shown that this proportionality is also observed for natural water with an unknown mixture of organic compounds.

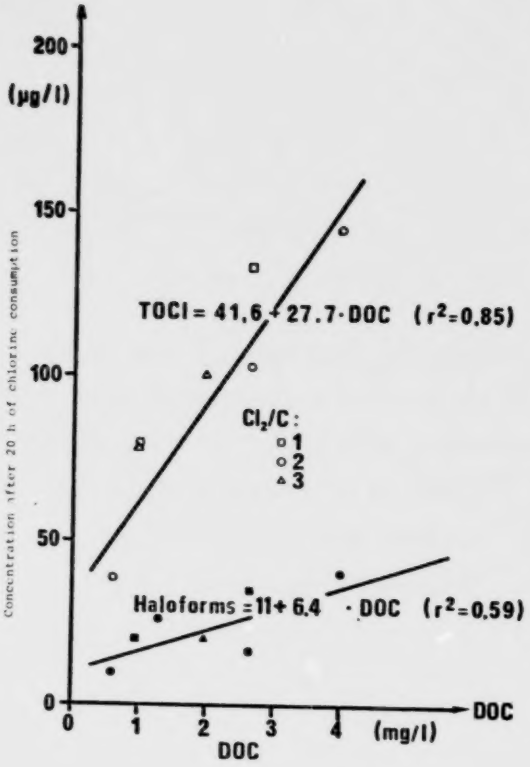


Fig. 7

TOCl and haloform formation in dependence on the DOC for various Cl_2/C ratios (reaction time 20 h)

6. Application of the method

The practicability of this method of continual chlorine-consumption measurements was checked in the period of June to August 1978 on numerous water samples from the eutrophic Wahnbach auxiliary dam, on the filtrate from the phosphorus-elimination plant, and on water samples from the mesotrophic Wahnbach dam itself. In addition, during the same period corresponding trials were performed on water samples from the Rhine at Bonn to determine whether this process is also applicable to surface waters polluted not only by domestic sewage but also by industrial effluents.

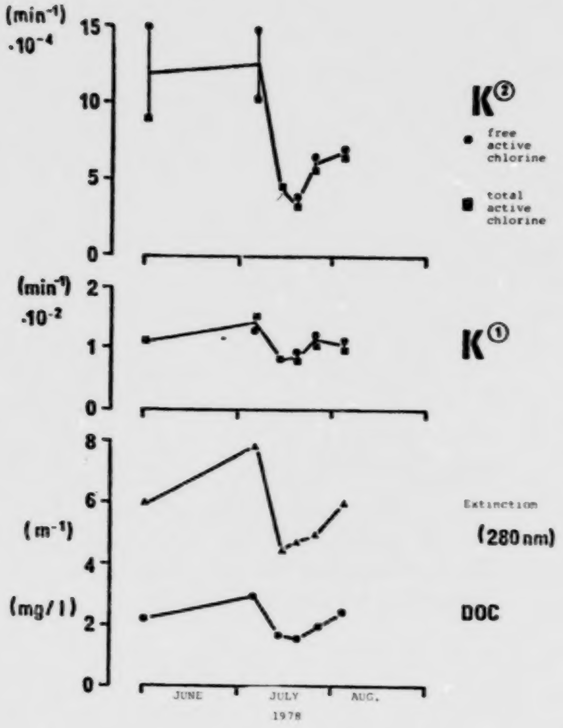


Fig. 8

Time variation of the usual quantities in comparison with the chlorine consumption rate constants K①and K② in water samples from the Wahnbach auxiliary dam

Fig. 8 shows the rate constants from the chlorine consumption measurements on water samples from the Wahnbach auxiliary dam for the investigation period. They are compared with the UV extinctions at 280 nm and with the DOC contents in these water samples. A really good correspondence of the course of the rate constants K^1 and K^2 and the sum parameters of UV extinction and the DOC can be seen. In both cases the rate constants obtained were plotted on the diagram as they resulted from the concentration changes in free active and total active chlorine. With the exception of two measured points, these K-values hardly differ from one another. It should be noted in this context that in June 1978 there were still analytical difficulties in the performance of continual chlorine-consumption measurements, and for this reason only one value was available for June.

If all the K^1 and K^2 values obtained in this period for the three waters are plotted against the UV extinction at 280 nm (see Fig. 9), a clear dependence on the concentration of the dissolved organic substances responsible for the UV extinction is observed, especially in the case of the constant K^2 of the slow reaction. The values for the auxiliary dam water to the right of the broken line in Fig. 9 approximately continue the course of the measurements from the other samples. However, no straight regression line can be drawn through these points, since at present there are still not enough measurements for extinctions greater than 6 m^{-1}.

On the other hand, the connection between the rate constant of the fast reaction K^1 and the content of organic substances in the water, that cause the UV extinction at 280 nm, is not so clear. A dependence appears to exist for the auxiliary dam water (to the right of the broken line) but not for the water samples from the filtrate of the phosphorus-elimination plant and the Wahnbach dam itself (left of the broken line). A possible explanation may be that during the treatment of the auxiliary dam water, rich in algae and humic materials, a selection of the organic substances takes place, in which the high-molecular materials are preferentially removed from the water, causing a proportional increase of the low-molecular organic compounds in the filtrate of the elimination plant and therefore also in the Wahnbach dam (7). Further studies will show to what extent there is a dependence of the chlorine reaction rate on the molecular weight range of the organic substances present in the water.

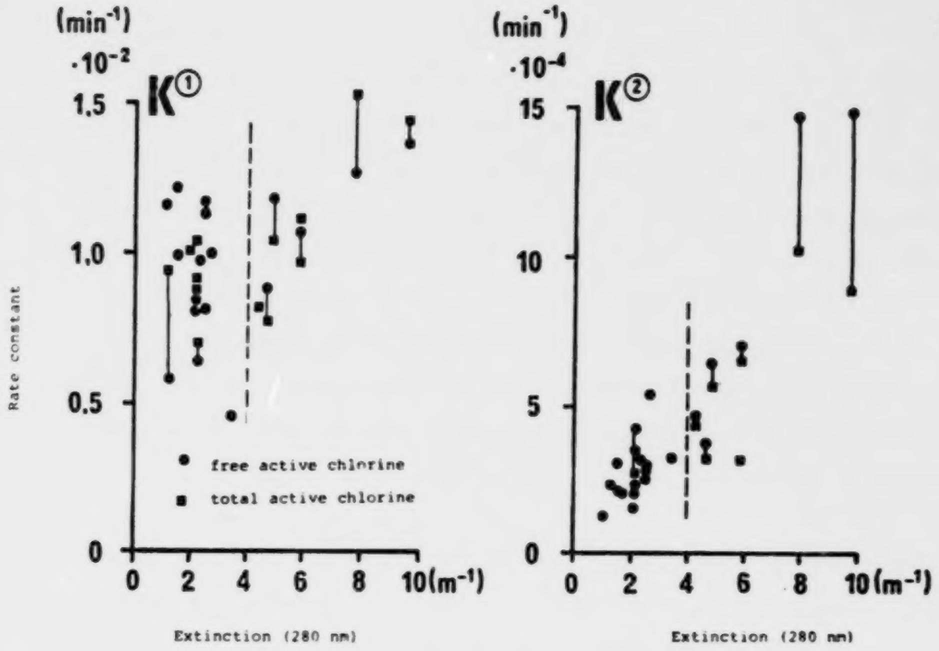


Fig. 9 Rate constants of the fast (K①) and slow (K②) chlorine consumption reaction plotted against the UV extinction of water samples from the Wahnbach auxiliary dam, from the filtrate of the P-elimination plant, and from the Wahnbach dam (June-August 1978)

Fig. 10 gives the results of experiments on Rhine water samples for the period June to August 1978. Changes in the rate constants for the slow (K^1) and fast (K^2) chlorine-consumption reactions are plotted, obtained from the concentration changes of free active and total active chlorine, as well as the UV extinction at 280 nm and the DOC content. To facilitate an interpretation of the results, the river flow of the Rhine during this period has also been plotted. Here too a relatively good parallel is evident between the individual quantities, but most of all between the UV values and the K^1.

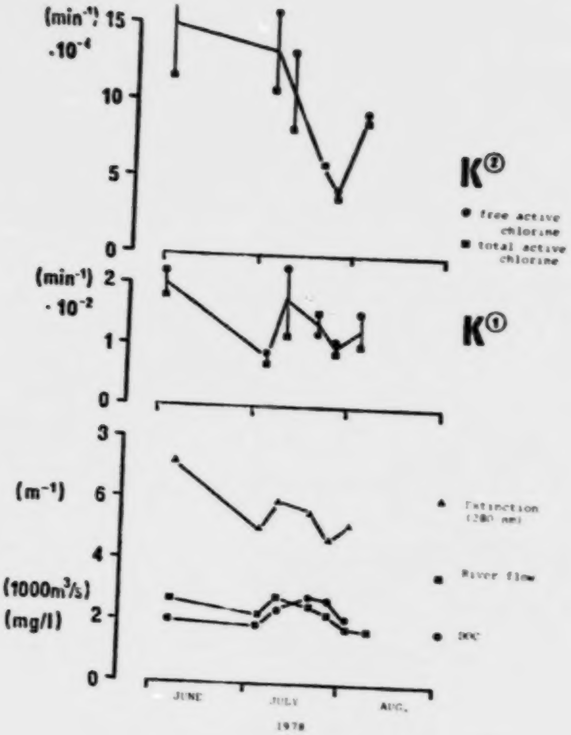


Fig. 10 Time variation of the usual quantities in comparison with the chlorine consumption rate constants K① and K② in water samples from the Rhine at Bonn

If the K^1 or K^2 values of these Rhine water samples are plotted against the UV extinction at 280 nm (Fig. 11), a connection also appears. Increasing concentrations of organic substances, which cause UV extinction, lead to an increase of the rate constants of the chlorine consumption. Remarkably, in the Rhine water samples at the same extinctions the K^1 values are about twice those in the water samples from the Wahnbach dam system.

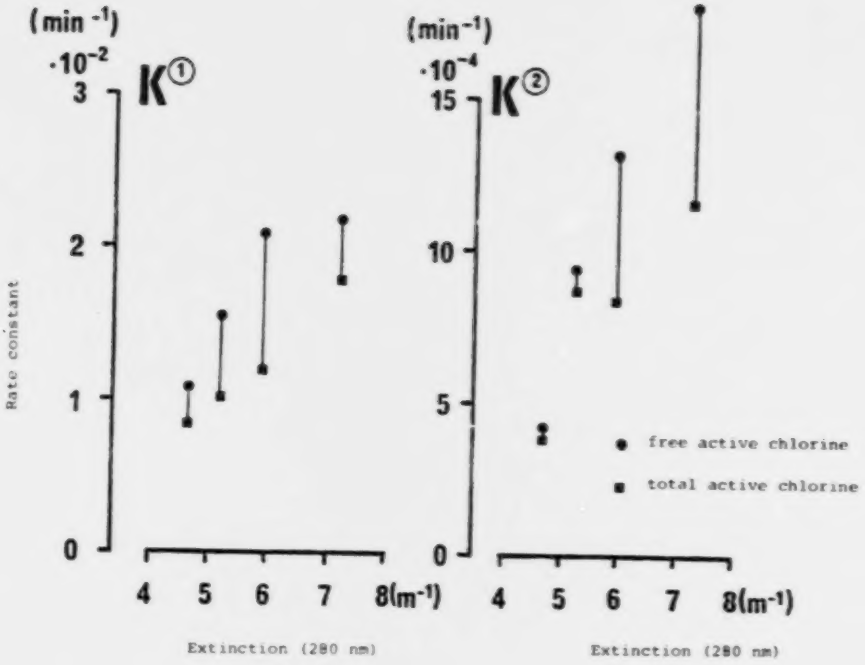


Fig. 11 Rate constants of the fast K ① and the slow K ② chlorine consumption reaction plotted against the UV extinction of water samples from the Rhine at Bonn (June-August 1978)

7. Connection between the rate constants and the formation potential for organochlorine compounds

In Fig. 7 the proportionality between the formation potential of organochlorine compounds and the content of organic solved compounds was clarified in the light of experiments with the prepared humic acid from auxiliary dam water. Similar experiments were performed on water samples from the Wahnbach auxiliary dam, the Wahnbach dam itself, and the filtrate of the phosphorus-elimination plant. The results are reproduced in Fig. 12. Here too, like in Fig.7, there is a really good correlation between the amount of TOCl or haloforms formed after a reaction time of 20 h and the content of organic substances causing UV extinction in the water samples (values to the right of the broken line : Wahnbach auxiliary dam). Such a connection is also found for water samples from the Rhine. It is noticeable that in the water samples from the Wahnbach dam itself (left of the broken line) the essential part of the TOCl is due to haloforms

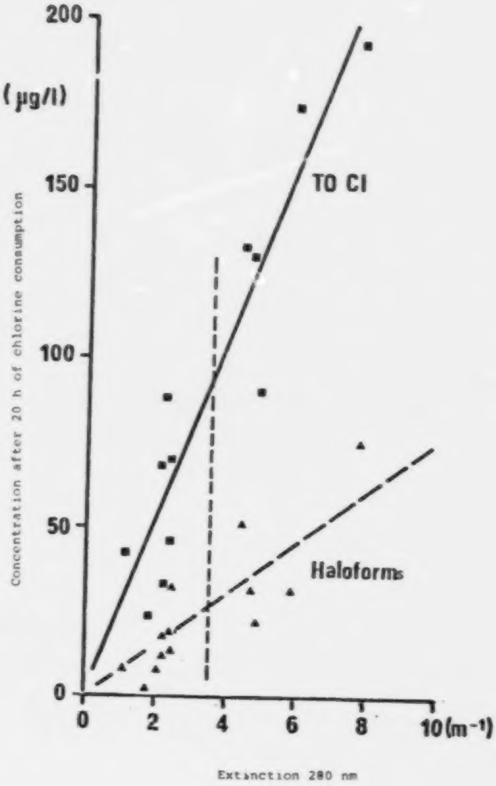


Fig. 12

TOCl and haloform formation potential in dependence on UV extinction in water samples from the auxiliary dam, main dam, and filtrate from the P-elimination plant

If the rate constants K^2 for the slow reaction are plotted against the corresponding concentrations of organochlorine compounds (TOCl and haloforms) formed by the chlorine-consumption reaction, a clear dependence is again observed. The amount of TOCl formed and of haloforms increases with increasing reaction rate, but not without limit, as can be seen from the exponential course of the curve for the

K^2 - TOCl system in Fig. 13. On the other hand, this connection is not so clear for the fast reaction, expressed by the constant K^1 (see Fig. 14).

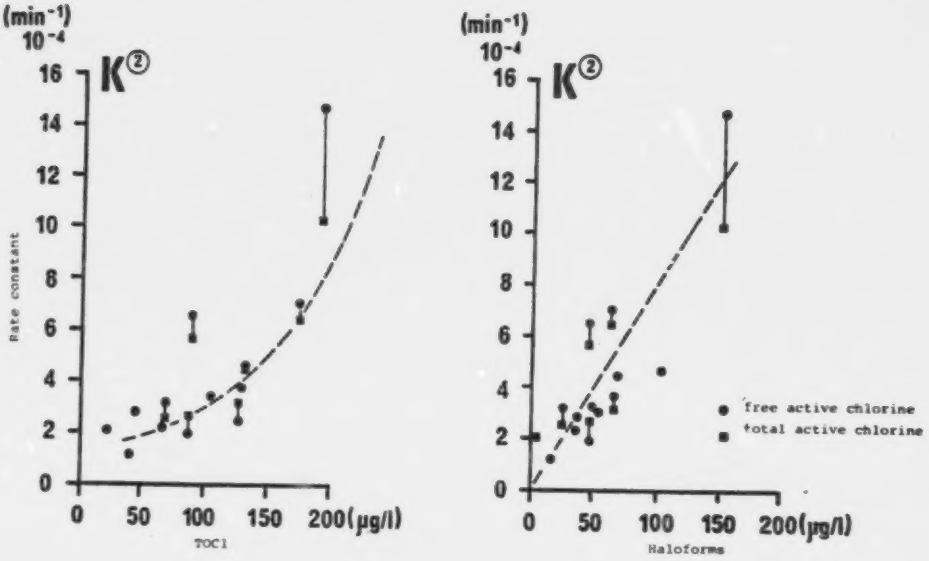


Fig. 13 Connection between the slow chlorine-consumption reaction ② (rate constant K②) and the formation of organic chlorine compounds (TOCl) and haloforms in water samples from the Wahnbach auxiliary dam, the filtrate of the P-elimination plant, and the Wahnbach dam (June-August 1978)

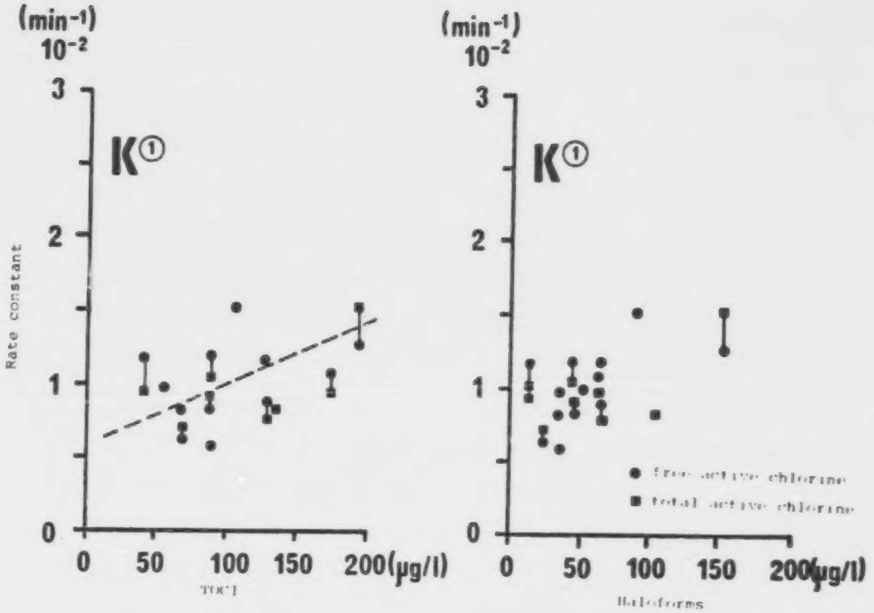


Fig. 14 Connection between the fast chlorine-consumption reaction ① (rate constant K①) and the formation of organic chlorine compounds (TOCl) and haloforms in water samples from the Wahnbach auxiliary dam, the filtrate from the P-elimination plant and the main Wahnbach dam (June-August 1978)

From these results the over-all conclusion can be drawn that within certain limits when the extent of the formation of organochlorine compounds is greater, the faster is the chlorine consumption reaction in a water sample. Detailed investigations on this entire complex are, however, still outstanding.

8. Experiments on chlorine consumption with algal suspensions and algal culture filtrates

The organic substances released by algae, insofar as they have a saccharide structure, respond only inadequately to the DOC determination used by us with UV oxidation (8). Depending on the algal species, DOC values that are essentially too low are obtained under certain circumstances, so that the chlorine-carbon ratio for the continual chlorine consumption measurement cannot be sufficiently securely established, for which reason preliminary experiments to obtain the expected chlorine consumption are advised. On account of the associated uncertainty of the values obtained we have as yet made no statements on the evaluation of the chlorine consumption rate, although differences dependent on the algal type can be discerned. A comparison of the chlorine-consumption kinetics for algal suspensions and algal membrane filtrates shows differences that may well be connected with the stability of the algal particles, although the course of the consumption is essentially similar. Further investigations on this are envisaged, which should also take into account the age and the stage of the algal culture.

Formation of organochlorine compounds by chlorination of algal cultures and algal culture filtrates

Fig. 15 shows the course of the TOCl formation plotted against the reaction time of the chlorine consumption, for suspensions of some algal species*. The particulate organic carbon (POC) content in these trials was approximately 60 mg/l; the Pseudanabaena suspension contained only 40 mg POC/l. The TOCl formation with this alga was very pronounced and, referred to particulate organic carbon, nearly double that with the green algae Carteria and Pandorina which were also studied. The siliceous alga Fragilaria, on the other hand, has the lowest TOCl-formation potential. A corresponding series of measurements with water from the Wahnbach auxiliary dam of 6.7.1978 fits in well with these data. At that time

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*The strains used came from the collection in the Biological Laboratory of the WTV, isolated by Dr. Clasen:

Fragilaria crotonensis	C 68/6
Carteria radiosa	C 69/15
Pandorina morum	C 72/2
Pseudanabaena galeata	C 67/2

the algal population had risen to 200,000 individuals/ml, consisting chiefly of microalgae and flagellates. It is typical for all algal species that the bulk of the TOCl -- nearly 90% -- is formed in the first 5 h of the chlorine reaction.

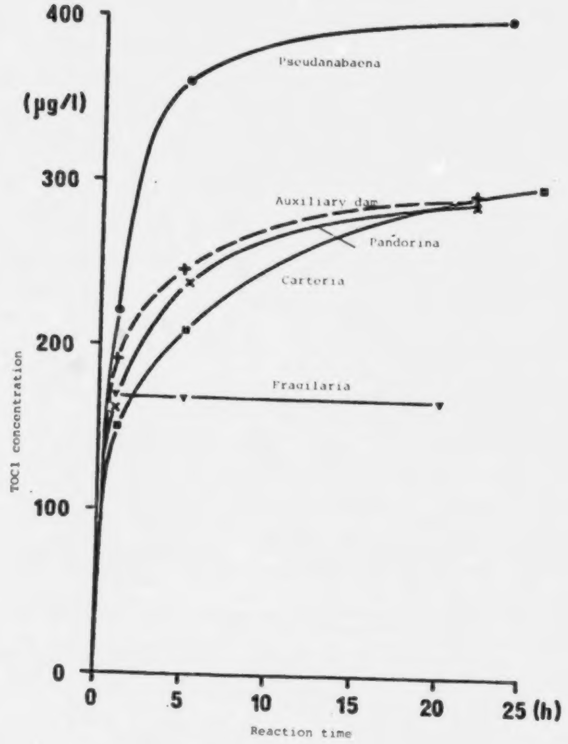


Fig. 15

TOCl as a function of the chlorine consumption time in unfiltered algal cultures and in auxiliary dam water during an algal bloom (200,000 individuals/ml)

If, however, the haloform formation is plotted against the reaction time of the chlorine consumption (Fig. 16), it is noted that, with the exception of the Fragilaria suspension and the auxiliary dam water, the amounts of haloforms produced in this series of experiments are only small and even begin to decrease with longer reaction times. This could be due to the fact that the haloforms formed are bound to the algal particles and to the cell fragments (detritus) produced by the chlorination, and are therefore not susceptible to the pentane extraction used for the determination of the haloforms. This explanation is supported by the fact that no decrease of the haloforms is observed in the case of the siliceous alga Fragilaria, which is very readily attacked by chlorination, and in the case of the microalgae predominating in the auxiliary dam water during the investigation period. This could yield indications on the treatment of water for drinking water with respect to the removal of haloforms by particulate organic substances (detritus) that can be flocculated and filtered off.

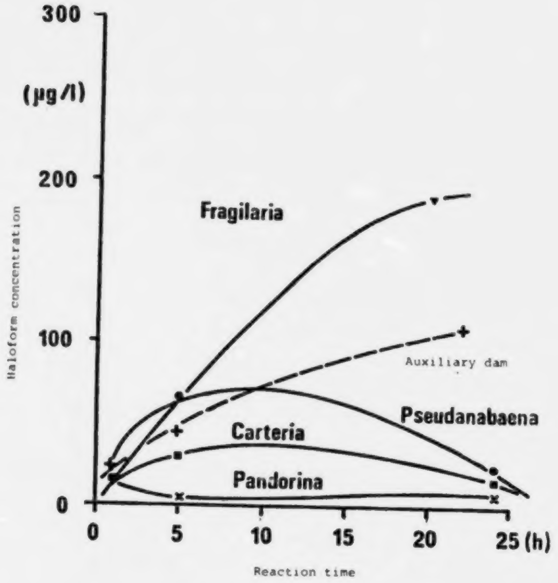


Fig. 16

Haloform formation as a function of the chlorine consumption time in unfiltered algal cultures and in auxiliary dam water during an algal bloom (300,000 individuals/ml)

To give a general view of the situation, we compared (see Table 1) the production of organic chlorine compounds in unfiltered algal samples with the production of organic chlorine compounds in similar algal samples that had undergone membrane filtration. The last two columns on the right of this table contain the percentage TOCl and the proportion of haloforms after 20 h of chlorine reaction time in the filtered samples, referred to the TOCl and haloform content in the corresponding unfiltered samples. While the TOCl-formation potential in the membrane-filtered samples is lowered by about 50%, the haloform-formation potential in the membrane-filtered samples is several times that in the unfiltered samples. Fragilaria is again an exception; here there is a decrease to about 30%.

TABLE 1 TOCl and haloform-formation potential (20 h reaction time) in algal suspensions in comparison with the corresponding membrane filtrates (0.45 μm)

Sample	Species of alga	unfiltered			membrane-filtered				
		POC mg/l	TOC l μg/l	Halof. μg/l	DOC mg/l	TOC l μg/l	Halof. μg/l	TOC l %unf.	Halof. %unf.
Fragilaria (14.6)	Siliceous alga	57	265	174	(1.7)	165	30	62	36
Fragilaria (3.7)	Siliceous alga	62	166	192	2.1	87	32	52	27
Pseudanabaena	Blue alga	40	400	22	(1.1)	173	106	43	480
Carteria	Green alga	63	300	18	5.0	155	92	52	510
Pandorina	Green alga	57	290	6	6.5	165	44	57	730
Auxiliary dam (6.7.78)	Mikroalgae	-	292	106	2.9	151	197	52	186

These figures show how different the effects of chlorination on the production of organic chlorine compounds can be with different algal species. About 0.5 - 1% of TOCl was produced with respect to the particulate organic carbon, and about 10% with respect to the DOC. The proportion of haloforms in the TOCl in the membrane-filtered alga waters varied quite considerably from alga to alga (about 20 - 60%), and in these experiments had a mean value of 40%. This high proportion of haloforms in the TOCl, produced by chlorination of membrane-filtered alga waters, is in accord with the relevant results for water samples from the Wahnbach auxiliary dam, the dam itself, and the filtrate from the phosphorus elimination plant.

Summary

From the time variation of the residual content of total and free active chlorine conclusions may be drawn about the content of organic chlorine-consuming substances in a water. To the water sample to be evaluated a sufficient amount of chlorine is added, appropriate to the content of organic substances present in the sample, expressed as the DOC. With the aid of an automatic analyzer the concentrations of total and free active chlorine were determined over a period of 20 - 24 h by continual measurements using the DPD method. If the chlorine content so obtained is plotted semi-logarithmically against time, the chlorine consumption course can be represented by two superimposed first-order reactions whose rate constants K^1 and K^2 are in the ranges of 10^{-2} and 10^{-4} min^{-1}. The spontaneous chlorine consumption, which takes place immediately after the chlorine has been added, and the time variation of which cannot be measured by the procedure used, is not considered here.

The rate constants K^1 and K^2 obtained in this way describe the course of the chlorine consumption by the water concerned and permit a characterization of its loading with organic chlorine-consuming substances. Inorganic chlorine-consuming substances, and in particular ammonium ions, did not interfere in the concentration ranges normally encountered in surface waters. With the aid of continual measurements of the chlorine consumption, unloaded waters, for example, can be clearly distinguished from anthropogenically or biogenically loaded surface waters, the algal substances present in these waters as a result of widely occurring bioprocesses also being covered.

Experiments were carried out to establish to what extent the rate constants change in dependence on the fixed Cl_2 : C ratio in the range of 1 - 3 with increasing DOC concentrations. It was found that the rate constant of the first fast reaction

(K^1) for Cl_2 : C ratios (concentration ratios) of 2 or 3 in the region 1 - 4 mg DOC/l is more or less constant, while the rate constants for the subsequent slow chlorine consumption (K^2) is very strongly dependent on the initial Cl_2 : C ratio and is only constant for Cl_2 : C ratios greater than 2.

In the light of this knowledge, reaction rate constants K^1 and K^2 were obtained for water from the auxiliary dam of the Wahnbach dam, for the filtrate from the phosphorus-elimination plant, for water from the Wahnbach dam, and for Rhine water (period of June to August 1978). Clear differences were found between the constants K^1 and K^2 in these cases. The constants K^1 and K^2 are proportional to the UV extinction at 280 nm measured in each case, showing that the chlorine consumption is due above all to the substances responsible for the UV absorption. From the proportionality between UV extinction as a parameter for the description of the "precursor concentration" on the one hand and the rate constants K^1 and K^2 on the other it follows that a proportionality must also exist with the organic chlorine compounds formed as the final reaction products -- TOCl and haloforms. This relationship could be established both for humic acids isolated from the auxiliary dam and for the various waters of our dam system. In exactly the same way, a connection exists between the rate of the chlorine-consumption reaction and the concentration of organic chlorine compounds formed.

If chlorine is allowed to react in the described manner with unfiltered algal suspensions of Fragilaria as a representative of siliceous algae, Carteria as a representative of the green algae, and Pseudanabaena as a representative of the blue algae, then over a period of a few hours a very rapid increase of the TOCl concentration is observed, which approaches a limiting value in 12 - 24 h. Particularly Fragilaria, which as a siliceous alga is sensitive to chlorine, shows a very rapid rise in the TOCl concentration within the first few hours of reaction. If, on the other hand, the algal suspensions are membrane-filtered before the chlorine has been introduced, the final TOCl concentrations are only half as high. Accordingly, in the practice of water treatment it must be considered that treatment of a raw water rich in algae with large amounts of chlorine (preliminary and breakpoint chlorination) leads to higher TOCl concentrations than the treatment of a surface water that has already undergone flocculation and filtration, in which the concentration of algae has thereby been markedly reduced. The formation of haloforms during the treatment of various algal suspensions with chlorine proceeds with varying degrees of intensity, and it should be particularly indicated that in the analytical determination of haloforms interference is caused by cellular fat and oil substances, so that the haloform concentrations as measured appear to be low.

It has been shown that the extent of the formation of organic chlorine compounds above a certain minimum chlorine addition is independent of the Cl_2 : C-ratio if a sufficiently long reaction time is allowed. In practice this time is usually provided by the transport of the water to the consumer.

(1) BERNHARDT, H., WILHELMS, A.
Der Einfluß algenbürtiger organischer Verbindungen auf den Flockungsprozeß bei der Trinkwasseraufbereitung
Organische Verunreinigungen in der Umwelt - Erkennen, Bewerten, Vermindern, Erich Schmidt Verlag, Berlin (1978) 112-146

(2) BERNHARDT, H., HOYER, O., SCHELL, H.
Chlorzehrung als Parameter zur Beurteilung der Qualität eines Talsperrenwassers
2 (1978) (im Druck)

(3) MAIER, D., MÄCKLE, H.
Wirkung von Chlor auf natürliche und ozonte organische Wasserinhaltsstoffe
Vom Wasser 47 (1976), 379 & 397

(4) SCHELL, H., HOYER, O., BERGER, M.
Bestimmung des freien, und des gesamten, wirksamen Chlors mit dem Auto-Analyzer nach der DPD-Methode (Deutsche Einheits-Verfahren G 4)
Z. f. Wasser- und Abwasser-Forschung (im Druck)

(5) EBERLE, S.H., HOYER, O., KNOBEL, K.P., v. HODENBERG, S.
Analytische und präparative Abtrennung organischer Säuren aus Wasser mittels Trioktylamin
Kernforschungszentrum Karlsruhe KfK 2529 UF (1977)

(6) EBERLE, S.H., KNOBEL, K.P., v. HODENBERG, S.
Untersuchungen über den Einsatz der Diafiltration zur Analyse der organischen Substanzen des Wassers
Kernforschungszentrum Karlsruhe KfK 2695 UF (1978) (im Druck)

(7) BERNHARDT, H., CLASEN, J., HOYER, O., WILHELMS, A.
Untersuchungen zur Oligotrophierung der Wahnbachtalsperre - Ermittlung der derzeitigen Situation
DVGW-Schriftenreihe Wasser (1978) (im Druck)

(8) WÖLFEL, P., SONTHEIMER, H.
Ein neues Verfahren zur Bestimmung von organisch gebundenem Kohlenstoff im Wasser durch photochemische Oxidation
Vom Wasser 43 (1974), 315-325

THE PRACTICE OF CHLORINATION OF DRINKING WATER

H. Lamblin

In connection with the lectures during this session I should like in the following to make some remarks on the selection of the chlorination agents and on the moment of the addition of these agents during the treatment.

1. Chlorination as a stage in the treatment of drinking water has been valued highly for a considerable time.

2. However, in more recent times analytical advances have directed the attention to by-products possibly exerting harmful effects.

3. A new philosophy is now arising in connection with chlorination.

   - One alternative to chlorination is a method that has already been very extensively investigated, i.e. the use of a new or already familiar chemical treatment agent that has sufficiently strong oxidizing and disinfecting properties, an effect that does not diminish with time and that eliminates ammoniacal nitrogen while at the same time giving harmless by-products.

   - A second way consists in first chlorinating actively pre-clarified water, i.e. water that essentially contains no further substances that could lead to the formation of undesirable by-products. A biological treatment prior to the chlorination can aid the purification of the water still further.

   - There is, however, a third way, which represents a compromise. This consists in establishing what are the most suitable points for the addition and which chlorination agents are most suitable for the existing treatment plants. The merit of this third variant lies in its possible rapid realization.

A number of external requirements that the water-treatment engineer must satisfy are already familiar:

a) the chemical elimination of the ammonia nitrogen may only take place after the elimination of the halomethane precursors,

b) the bactericidal action and the oxidation of the organic substances are clearly stronger when the water has been clarified beforehand,

c) certain organic substances not oxidized by chlorination can be made oxidizable either by an ozone treatment or by biological modification by passage through activated carbon filters or through other materials.

d) An after-chlorination may be necessary to maintain a good biological stability of the water in the distribution network, particularly in the case of large networks.

It can be assumed that good adaptation of the chlorination by one or more of the available chlorine derivatives, depending on the specific features of each case, and a careful choice of the time of addition in the individual stages of the treatment plant, largely make it possible to limit the formation of already known by-products and to ensure a high quality of the product water.

USE OF CHLORINE BY THE NETHERLANDS WATERWORKS

A.P. Meijers

In practice chlorine is used at different places in the purification system:

1. transport chlorination of raw water or partially treated water;
2. safety chlorination at the end of the purification process in order to avoid bacterial growth in the distribution system;
3. breakpoint chlorination, most often the first purification step, used for the oxidation of ammonia, some organics and finally disinfection;
4. process chlorination in order to avoid disturbances during the purification processes by biological activity;
5. finally, chlorine is used for the oxidation of iron II to iron III as a coagulant.

Except in the last application, chlorine is always used for disinfection, which process must indeed be considered as the most important step in drinking water purification.

In order to be informed about the use of chlorine, a questionnaire was sent to a number of selected Dutch waterworks in April of last year. (Ref.(I) Problematiek haloformen Meded., nr. 57, KIWA, mei 1978) From the results of the questionnaire it was concluded that all surface-water processing waterworks use chlorine to some extent. The ground-waterworks (60 %) only use chlorine, incidentally. Transport chlorination was used by three big waterworks serving Amsterdam, Rotterdam, The Hague and North Holland.

In these cases the water is chlorinated after partial purification with 2 to 4 g/m^3 of chlorine and transported for about 40 kilometers for additional purification. In the summer more chlorine is needed for this purpose than in the winter.

Breakpoint chlorination is used by several waterworks, for instance in the Berenplaat works at Rotterdam.

As the surface-water processing waterworks have safety chlorination at the end at a level of 0.5 g/m^3, not only chlorine gas is used but also sodium chlorite, and at some places chlorine dioxide.

Furthermore, it was clear that surface-water processing waterworks, which include artificial recharge in the dunes as a purification step, do not use breakpoint chlorination.

However, before artificial recharge in the dunes, transport chlorination took place.

Nevertheless, there are still four waterworks processing surface water not taken from the river Rhine nor the river Maas, which do not add chlorine for transportation nor for breakpoint chlorination.

In summary, in one third of the produced water in the Netherlands transport chlorination was included (800 tons), 10 % to 15 % was treated by breakpoint chlorination (650 tons). For iron oxidation 430 tons of chlorine were used, and for safety chlorination for all waterworks only 200 tons was used.

Thus most of the chlorine is used for transport- and for breakpoint chlorination at only a limited number of large waterworks. Therefore, the aim in the Netherlands, in order to limit the use of chlorine, is to search for possible alternatives in these cases.

This includes especially a better treatment before transportation so that the use of chlorine will not be necessary, removal of ammonia by biological filtration in order to avoid breakpoint chlorination, no use of Fe II as a coagulant, and finally the use of an alternative disinfectant.

However, all of these measures will involve considerable consequences for the waterworks in question.

THE PRACTICE OF CHLORINATION OF DRINKING WATER

G. Uhlig

The practical engineer often comes across an apparently surprising phenomena concerning the chlorine requirement and the chlorine consumption, of raw waters, when the treatment consists of a biologically working activated carbon filtration. This effects the so-called nitrification process, i.e. a microbiological oxidation of the ammonia nitrogen to nitrate nitrogen. Stoichiometrically, 2 1/2 moles of oxygen per mole of ammonium or 3.6 mg of oxygen per mg of ammonium are necessary for this purpose. This has the following consequences in chlorination practice:

1. If the oxygen content of the raw water is insufficient, the nitrification is not completed, proceeding only to the stage of nitrite, which (in addition to the breakthrough of ammonium) gives rise to a particularly high chlorine consumption in accordance with the reaction

$$NO_2^- + HOCl \longrightarrow NO_3^- + HCl.$$

2. Even when the oxygen content of the raw water remains the same, an activated carbon filter must sometimes be temporarily shut down for operational reasons. After a few hours the biology of the filter is upset owing to the lack of oxygen and the result is a sudden rise in ammonium and nitrite when the filter resumes operation. After the shutdown of an activated carbon filter for only 48 h we measured a nitrite content of 1.3 mg/l.

On account of the potential danger of the production of the extremely carcinogenic nitrosamines, it is advisable in such cases to reconnect the filter to the drinking water supply only under laboratory control after back-washing and drainage of a suitable amount of first filtrate. This situation is otherwise signalled by a sudden rise in the chlorine consumption resulting in disturbed chlorine measurements with the same infeed.

Special problems inevitably arise when, for example, the shutdown of a whole activated carbon filter plant consisting of many units becomes necessary for operational reasons. Considerable amounts of first filtrate may have to be discarded if it is not possible to continue operating the filter at least with a minimum throughput of oxygen-rich water in forward or back motion.

3. Even after the filters have been recharged with fresh or reactivated carbon, it can take many days before the biology on the carbon develops its full activity. Here too the outcome is a strongly elevated chlorine consumption of the water if such filters are prematurely connected to the drinking water network.

4. In addition,the function of some of the equipment for continuous chlorine indication is strongly pH-dependent, and at pH above about 7.5 free chlorine can no longer be indicated unless an acid or buffer solution is added continuously to the water.

However, before filters freshly charged with reactivated carbon are put in operation, initial pH levels of 10-12 can still be measured, presumably caused by oxides and carbonates formed during reactivation of the carbon, depending on the salt content of the water with which the carbon was previously wetted, from the cations of these salts.

FORMATION OF NON-POLAR ORGANO-CHLORO COMPOUNDS AS BYPRODUCTS OF CHLORINATION

A.A. Stevens

The Conference Committee has assigned to me the task of reviewing the formation of "non-polar" byproducts of chlorination of drinking water. For the purposes of this paper, the term "non-polar" applies to that group of individual compounds that can be separated from dilute aqueous solution by solvent extraction or gas stripping, i.e. compounds of relatively low water solubility. The final method of analysis is always gas phase chromotography, further restricting this discussion to compounds volatile at those temperatures.

I. Early experience

Before the 1970's little was known about the formation of individual halogen substituted organic compounds during chlorination for drinking water disinfection. Knowledge and consideration of byproducts was limited to the recognition of halogen substitution on nitrogenous compounds as possible contributors to "combined chlorine" (chloramines) and chlorophenolic byproducts as causes of tastes and odors in some problem supplies.

II. Trihalomethanes

Not until modern analytical techniques were applied to finished drinking water and companion raw water samples did the list of known byproducts of chlorination begin to grow. In December of 1974, independently, Rook (1) and Bellar, et al. (2) reported the formation of chloroform and other chlorine- and bromine-substituded trihalomethanes during drinking water treatment as a direct result of the chlorination-disinfection practice. Partly because of these discoveries, the United States Environmental Protection Agency (USEPA) undertook a survey of 80 selected cities to measure the concentrations of six halogenated compounds in raw and finished water (3). Those six included the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, bromoform) suspected of being formed during chlorination, plus carbon tetrachloride and 1,2-dichloroethane, known contaminants at some locations, but not necessarily formed on chlorination. During this National Organics Reconnaissance Survey (NORS) the occurrence of trihalomethanes in finished drinking water was demonstrated to be widespread and a direct result of the chlorination practice. No hard evidence was found in this regard with respect to 1,2-dichloroethane or carbon tetrachloride. More recent surveys conducted by USEPA and others have not resulted in a change of this conclusion regarding the haloforms, although CCl_4 has since been found to be an occasional significant contaminant of Cl_2.

Based on the survey results, a theoretical finished water with the median concentration of each compound would contain about 21 μg/l of chloroform, 6 μg/l of bromodichloromethane, 1.2 μg/l of dibromochloromethane, and an amount less than the detection limit for the method used of bromoform (Fig. 1). Although most of the finished waters tested demonstrated this decreasing order of concentration, this was not always the case. The finished water at one location had a chloroform concentration of only 12 μg/l, but a bromoform concentration of 92 μg/l. This high concentration of bromoform was suspected to reflect a relatively high bromide concentration in the raw water (see below). Even though more recent information indicates a preponderance of yet unidentified organic-substituted halogen, measured as "organic halogen" in some form (4), the trihalomethanes are present in the highest concentrations of non-polar species resulting from chlorination of drinking water individually identified to date (September 1978).

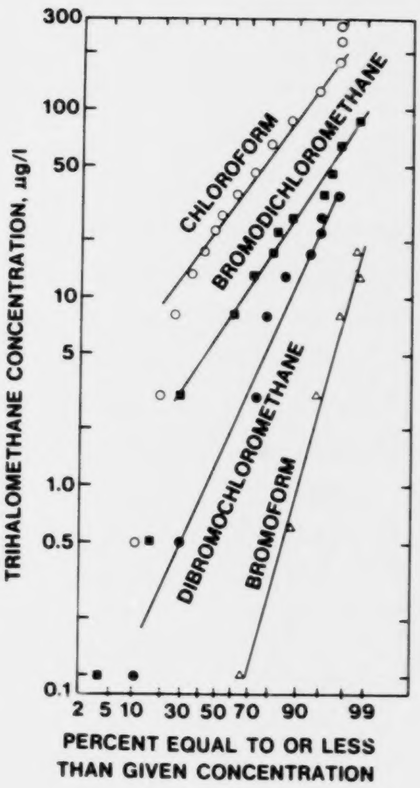


Fig 1 Frequency distribution of trihalomethane data. NORS

Because of findings concerning the carcinogenicity (5) of chloroform the USEPA has proposed an interim Primary Regulation for trihalomethanes in consumers' drinking water of 0.10 mg/l total trihalomethanes ($CHCl_3$, $CHCl_2Br$, $CHBr_2Cl$, and $CHBr_3$). At many water utilities, specific new or improved treatments will be required to reduce existing concentrations of trihalomethanes to meet this standard. Indeed, the continued heavy use of chlorine for drinking water disinfection is now being questioned in the USA.

Factors influencing trihalomethane formation

The formation of trihalomethanes during chlorination of drinking water now seems to be well accepted to result from a complicated mechanism of attack by aqueous halogen species on natural aquatic humic substances (humic and fulvic acids) and not usually significant from sources of industrial water pollution (1,6,7,8).

Design of the most effective treatment strategy depends on a good knowledge of factors influencing trihalomethane formation. Two factors, however, that have a strong influence on trihalomethane concentrations over which the water treatment plant operator has little or no control under most circumstances are temperature and Br^- or I^- concentration.

Temperature

Figure 2 clearly demonstrates the positive effect of increasing temperature on trihalomethane formation upon chlorination of Ohio River water in the laboratory (7). A corresponding seasonal variation is noticed at a water utility using that same source and has been shown to be largely a temperature effect (10). Thus treatment problems become more acute during seasons of higher ambient temperature causing higher water temperatures during treatment and distribution.

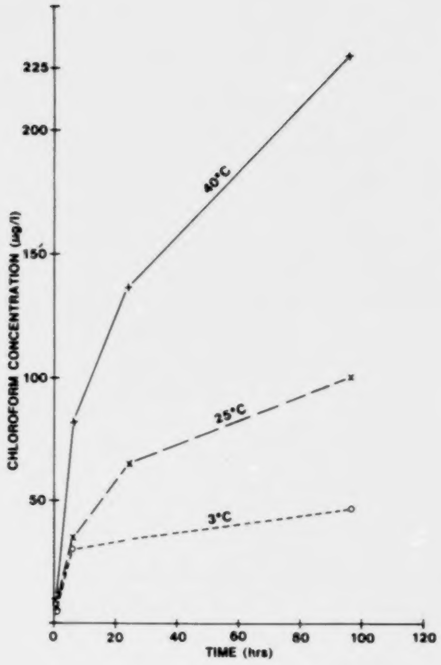


Fig. 2

Chloroform production at three temperatures raw water 10 mg/l chlorine dose; pH 7

Bromide and iodide concentration

Bromide and iodide ions are oxidized by aqueous chlorine to species capable of participating in organic substitution reactions resulting in the formation of pure-and mixed halogen trihalomethanes. Bunn et al. (10) first confirmed one of the suspicions of Rook (1) that this could occur in aqueous systems when they chlorinated Missouri River water in the presence of added fluoride, bromide, and iodide and observed the formation of all ten possible chlorine, bromine, and iodine containing pure- and mixed halogen trihalomethanes. On a theoretical basis, fluorine substitution was not expected and was not observed. To date, at least six of these species have been found in finished drinking water (chloroform, bromodichloromethane, dibromochloromethane, bromoform, dichloroiodomethane, and bromochloroiodomethane) (11).

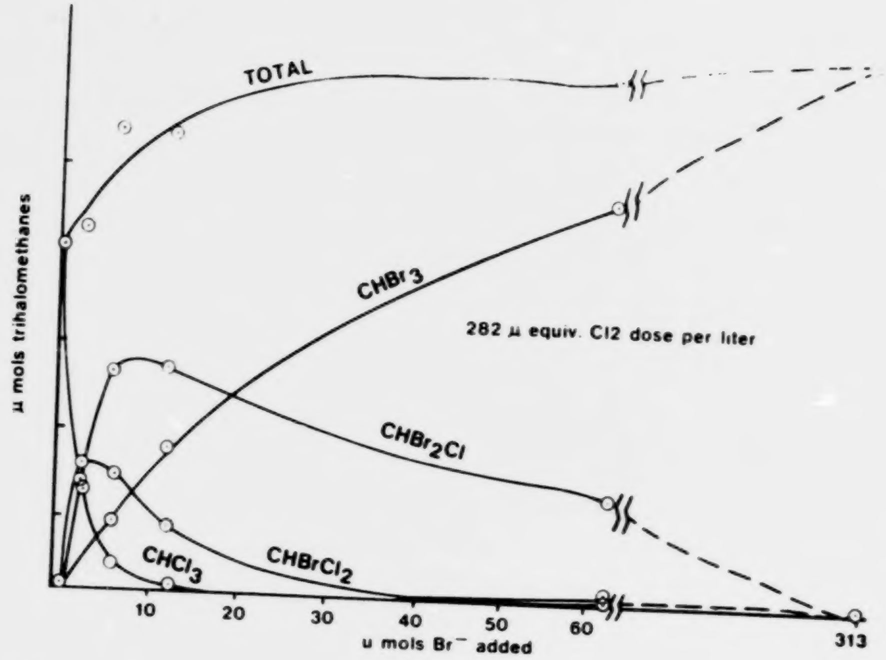


Fig. 3 Trihalomethanes formed by reaction of humic acid with aqueous chlorine in the presence of varying bromide ion

Figure 3 illustrates the results of work conducted in our laboratory on the effect of added bromide on the ratio of trihalomethanes produced during reaction of aqueous chlorine with humic acids. Note that bromine substitution is favored over chlorine even though chlorine is in large excess compared with the initial bromide. Additionally, the total molar yield of trihalomethanes increases with increasing bromine substitution. This was also observed when pure aqueous bromine was reacted with the humic acid under the same conditions as aqueous chlorine. Thus, bromine competes more effectively than chlorine for active sites on the humic acid precursor molecule, perhaps mechanistically by way of faster substitution reaction rate. This effect is so pronounced as to dramatically increase total haloform yields where bromide is present. Indeed, similar increases in total haloform yield have been reported to occur on chlorination of a bromide spiked natural water (11) and more importantly at a water treatment plant in the USA where sea water intrusion was temporarily responsible for increases in bromides (12) (Fig. 4). Thus, much more complete control of trihalomethane precursor, as one method of meeting proposed USEPA drinking water standards, is necessary when significant concentrations of bromide are present in the source water.

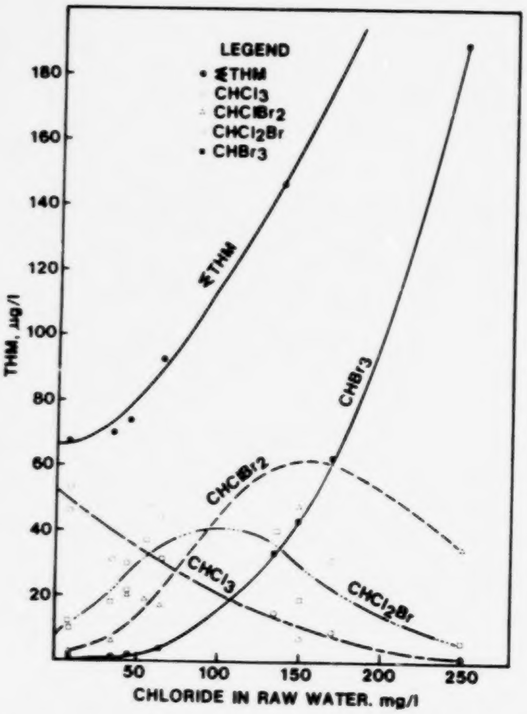


Fig. 4 Effect of salt water intrusion on THM formation potential (from Lange, 1978)

Effect of pH

Increasing the pH of the water being treated has been shown by numerous workers to dramatically influence rates of formation of haloforms during water treatment (Fig 5) (7). Control of pH during treatment before chlorination, such as recarbonation in a lime softening system, has been used in attempts to control haloform formation (13).

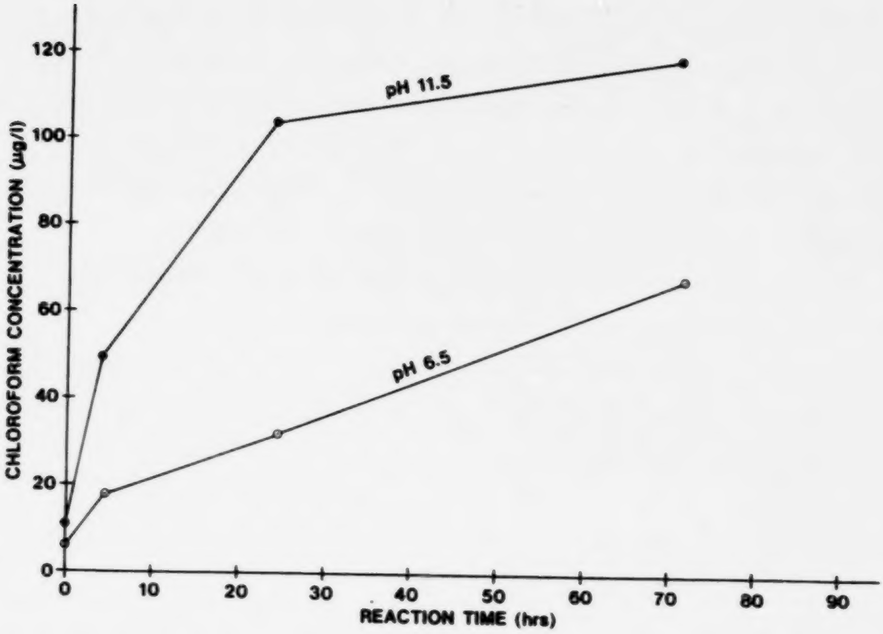


Fig. 5 Effect of pH on chloroform production, settled water 25°C, 10 mg/l chlorine dose

The increase of trihalomethane formation rate with pH was expected because the classical haloform reaction is base catalyzed; however, this explanation is likely to be an oversimplification where rather complex humic acid structures are involved. Simple methyl ketones, models for the haloform reaction, have been shown to react too slowly to account for trihalomethane formation under most drinking water conditions, suggesting a different reaction mechanism (7). Christman once suggested a simple "opening up" of the humic acid molecule because of mutual charge repulsion at high pH increasing the availability of more reactive sites on that molecule as a possible cause of the influence of high pH on reaction rate (Personal communication).

Characteristics and Concentration of Precursors

In artificial systems, increasing the concentration of humic acid precursor in the presence of excess chlorine with otherwise constant reaction conditions causes haloform yields to increase in direct proportion to the humic acid dose (Fig. 6) (7). From supply to supply, however, only crude relationships have been found between organic carbon concentrations and trihalomethane yields (3). Similar effects have been noted upon treatment. Further, rate curves seem to take on distinctly different shapes depending on the source of precursor substances. The work of Rook (8) shows the reaction of fulvic acid solutions to be characteristic of m-dihydroxyphenyl moieties (e.g. resorcinol) in that the reaction is nearly complete at near neutral pH in less than two hours (Fig. 7).

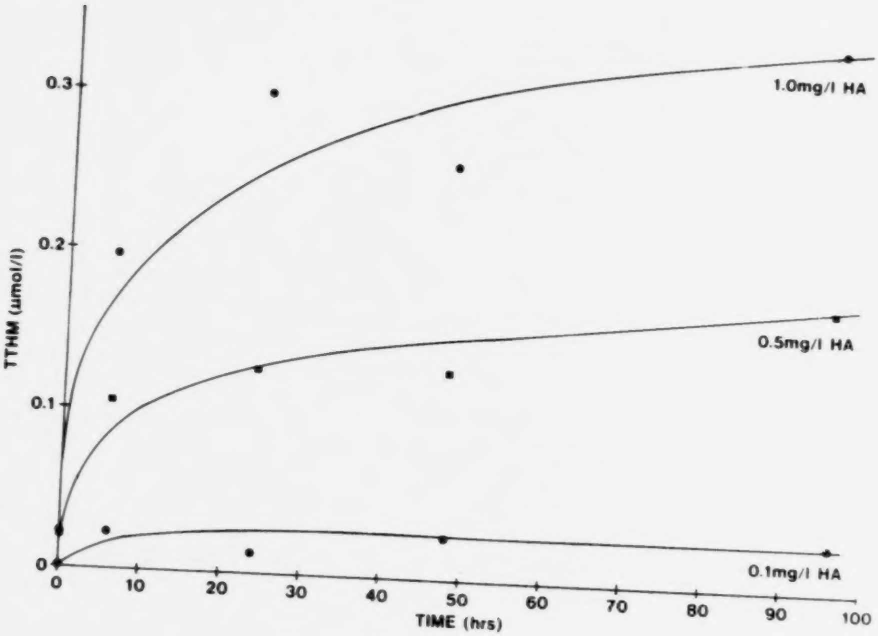


Fig. 6 Effect of humic acid concentration on trihalomethane production, pH 6.7; 25°C; 10 mg/l chlorine dose

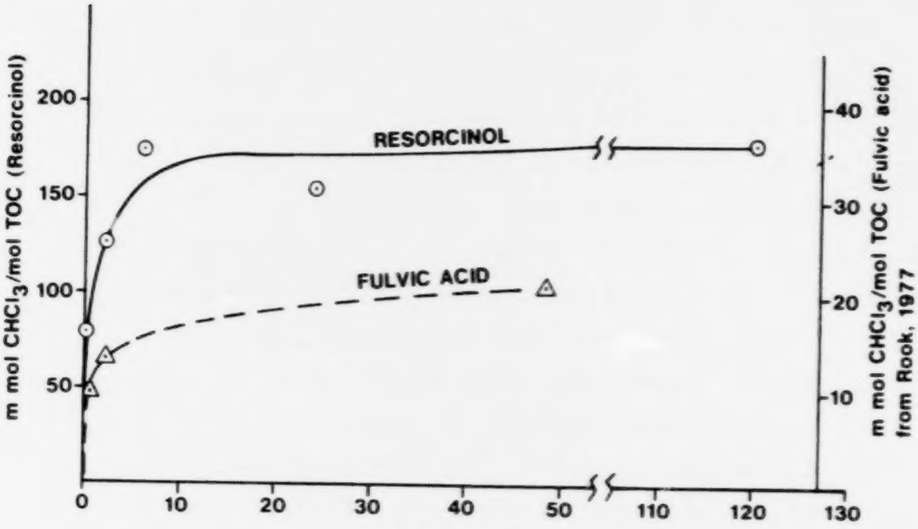


Fig. 7 Reaction of model precusors with aqueous chlorine

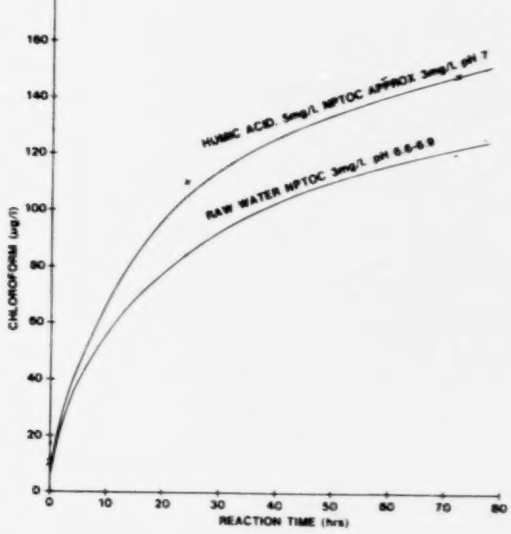


Fig. 8 Comparison of humic acid, raw water reaction rates at similar NPTOC concentrations, 10 mg/l chlorine dose

Quite a different characteristic curve is observed with Ohio River water precursor and a different source of humic acid under similar conditions where the reaction takes place relatively slowly over a period of many days (Fig. 8) (7). The probable differences in precursors at different locations has been further demonstrated in work at the EPA Cincinnati laboratory where, as expected, treatment with permanganate at low dosages was nearly 100 percent effective in preventing the formation of trihalomethanes on chlorination of resorcinol and m-dihydroxybenzoic acid solutions, yet permanganate was only marginally (10-20%) effective in reducing the ability of Ohio River precursors to form trihalomethanes upon subsequent chlorination.

Additionally, work at the Cincinnati laboratory has shown there to be only a slight influence on trihalomethane formation rate (or yield) of increasing chlorine dose (beyond demand) where "precursor" is kept constant (Fig. 9). Both similar and contrary results have been reported by others while working with different sources of precursors (6, personal communication). The above serves only to indicate that although precursor materials from various supplies may be of largely natural origin, the composition of that material is likely to be different, depending on the type of supply involved and the source of precursors in the water shed. Considerably more work is needed, therefore, to understand the complex mechanisms of trihalomethane formation during water chlorination and to determine whether water treatment strategies for control of THM's could vary significantly among these various supplies.

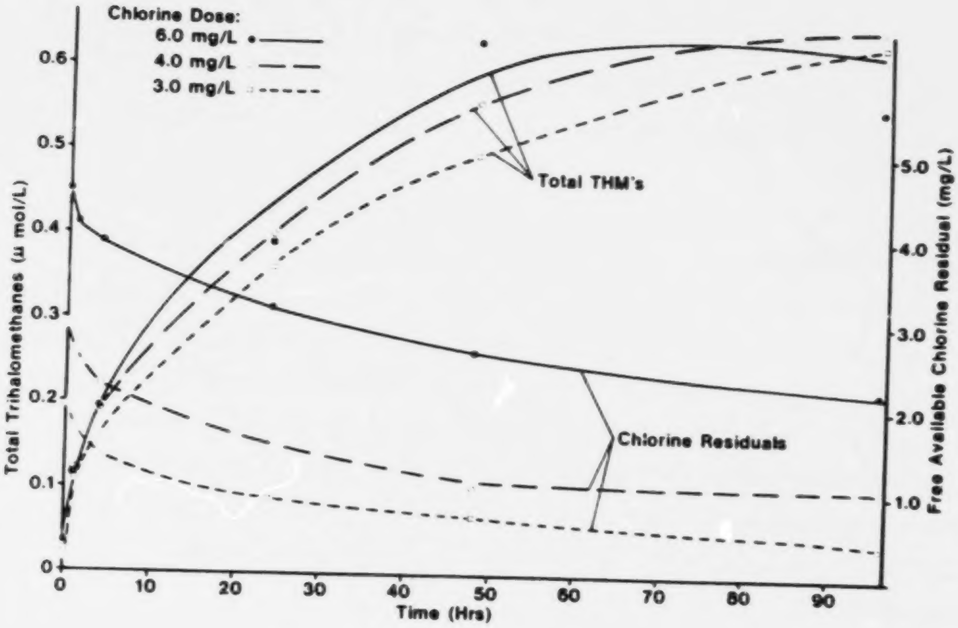


Fig. 9 Effect of chlorine dose on trihalomethane formation

III. Other identified apparent products of chlorination/treatment

As mentioned earlier, trihalomethanes represent the most important group of individual identified halogenated species from a concentration standpoint identified in finished drinking water and resulting from chlorination practice. Although the mechanisms for trihalomethane formation are not well understood, many of the conditions favoring or inhibiting trihalomethane formation have been established. Other non-polar compounds have been detected in finished water at the ng-µg/l level that were not detectable in the source water or present in lower concentrations. Most of the sources of these are even less well understood.

At least 19 non-trihalomethane halogenated volatile compounds have been shown by Rook (8) (Rotterdam Storage Reservoir) and more by Stieglitz, et al., (14) (Rhine River Bank Filtrate) to be formed at low concentrations upon chlorination. Rock speculates on a possible pathway to explain the formation of some of the observed byproducts in a way related to his proposed mechanism for haloform formation from m-dihydroxyphenyl moieties. Stieglitz suggests no mechanism. Coleman et al. (15) reported the co-presence of chloropicrin, chlorobenzene, a chlorotoluene isomer and a chloroxylene isomer with their respective logical precursors, nitromethane, benzene, toluene, and m-xylene, in finished chlorinated tap water. All of the above precursors but benzene were shown to be reactive with aqueous chlorine to form the expected products. More recently, chloroacetonitrile derivatives have been observed in a finished tap water as a result of work at the Cincinnati laboratory. Milligram per liter concentrations of acetonitrile could not be made to react with chlorine under realistic reaction conditions to form detectable chlorinated derivatives, however. Further, even simple aromatic hydrocarbons have been observed in some studies to be more prevalent or in higher concentrations in finished tap water than in the respective raw source water (16,17).

Considerable effort lies ahead to determine mechanisms for formation of these apparent byproducts of chlorination (or possibly other treatment in the latter cases) that in most cases seem to defy straightforward explanations.

IV. Summary

Modern analytical techniques have expanded our knowledge of the formation of unwanted by-products during chlorination of drinking water. Of the non-polar fraction, trihalomethanes typically are formed in the highest concentrations, and much is now known about factors influencing their formation. Other chlorinated and non-chlorinated non-polar apparent by-products have been observed, but little is known about their sources.

(1) ROOK, J.J.
Formation of Haloforms During Chlorination of Natural Waters
Water Treatm. and Exam. 23 (1974), 2, 234

(2) BELLAR, T.A., LICHTENBERG, J.J., KRONER, R.C.
The Occurrence of Organohalides in Chlorinated Drinking Water
J. AWWA 66 (1974), 11, 703

(3) SYMONS, J.M., BELLAR, T.A., CARSWELL, J.K., DeMARCO, J., KROPP, K.L., ROBECK, G.G., SEEGER, D.R., SLOCUM, C.J., SMITH, B.L., STEVENS, A.A.
National Organics Reconnaissance Survey for Halogenated Organics in Drinking Water
J. AWWA 67 (1975), 11, 634

(4) KÜHN, W., SONTHEIMER, H., KURZ, R.
Use of Ozone and Chlorine in Waterworks in the Federal Republic of Germany
Ozone/Chlorine Dioxide Oxidation Products of Organic Materials
Proceedings of Conference, International Ozone Institute, Cleveland, Ohio (1978), 426-442

(5) -
Report on the Carcinogenesis Bioassay of Chloroform
National Cancer Institute, Div. of Cancer Cause and Prevention, Washington, D.C. (1976)

(6) ROOK, J.J.
Haloforms in Drinking Water
J. AWWA 68 (1976), 3, 168

(7) STEVENS, A.A., SLOCUM, C.J., SEEGER, D.R., ROBECK, G.G.
Chlorination of Organics in Drinking Water
J. AWWA 68 (1976), 11, 615

(8) ROOK, J.J.
Chlorination Reactions of Fulvic Acids in Natural Waters
Environmental Science and Technology 11 (1977), 5, 478

(9) LOVE, O.T.
Drinking Water Research Div., Municipal Environmental Research Laboratory, US EPA, Cincinnati, Ohio
Unpublished data

(10) BUNN, W.W., HAAS, B.B., DEANE, E.R., KLEOPFER, R.D.
Formation of Trihalomethanes by Chlorination of Surface Water
Environmental Letters 10 (1975), 3, 205

(11) KLEOPFER, R.D.
Analysis of Drinking Water for Organic Compounds
Identification and Analysis of Organic Pollutants in Water, Ann Arbor Science, Ann Arbor, Michigan (1976), 399

(12) LANGE, A., KAWCRYNSKI, E.
Contra Costa County Water District Experience
Presented at the California - Nevada Section AWWA Seminar on Organics in Domestic Water Supplies, Palo Alto, CA, USA, April 12 (1978)

(13) SYMONS, J.M., STEVENS, A.A.
Physical-Chemical Pretreatment for the Removal of Precursors
Presented at Conference on Oxidation Techniques in Drinking Water Treatment at Karlsruhe, Federal Republic of Germany, Sept. 9-13 (1978)

(14) STIEGLITZ, L., ROTH, W., KÜHN, W., LEGER, W.
The Behavior of Organohalides in the Treatment of Drinking Water
Vom Wasser 47 (1976), 347

(15) COLEMAN, W.E., LINGG, R.D., MELTON, R.G., KOPFLER, F.C.
The Occurrence of Volatile Organics in Five Drinking Water Supplies Using Gas Chromatography/Mass Spectrometry
Identification and Analysis of Organic Pollutants in Water, Ann Arbor Science, Ann Arbor, Michigan (1976), 305

(16) SEEGER, D.R., SLOCUM, C.J., STEVENS, A.A.
GC/MS Analysis of Purgeable Contaminants in Source and Finished Drinking Water
Proceedings of 26th Annual Conference on Mass Spetrometry and Allied Topics, held in St. Louis, Missouri, May 28 - June 2 (1978)

(17) BRASS, H.J., FEIGE, M.A., HALLORAN, T., MELLO, J.W., MUNCH, D., THOMAS, R.F.
The National Organic Monitoring Survey: Samplings and Analysis for Purgeable Organic Compounds
Drinking Water Quality Enhancement Through Source Protection, Ann Arbor Science, Ann Arbor, Michigan (1977), 393

FORMATION AND BEHAVIOUR OF POLAR ORGANIC CHLORINE COMPOUNDS

W. Kühn and R. Sander

In the previous report, Dr. Stevens reported on non-polar organic chlorine compounds which can be formed in the chlorination of waters. The resolution of this subject into two components, i.e. into non-polar and polar chlorinated products, is not founded on their possible hygienic or toxicological differences but rather on the very different methods used for their analytical detection (1,2).

This class of compounds has recently attracted considerable interest not only because of its toxicity but because its study was first made possible by modern analytical methods. The phrase "a water is only as good as analysis permits" is particularly appropriate to the analysis of organics in water.

For this reason I should like to start with a careful consideration of the analytical treatment of this class of compounds.

As shown in Table 1, the treatment of organic chlorine compounds, which as a rule are present in microgram amounts, can be divided into an enrichment stage, separation into individual substances, and the actual determination. In practice, all polar organic chlorine compounds present analytical difficulties. In contrast to the usually low-molecular, non-polar, volatile compounds, on which the previous speaker reported, polar compounds are usually high-molecular, less volatile, and therefore more difficult to deal with. However, if a group of substances resists individual substance analysis, it is legitimate and sensible, and not only in water chemistry, to treat these substances by a general or group method. The method developed at the Engler-Bunte-Institute for the treatment of all the organic chlorine compounds (TOCl: total organic chlorine) begins with an adsorptive enrichment, followed by mineralization in pyrohydrolysis and subsequent detection of the now easily analysed chlorine (3-5).

TABLE 1 Treatment of halogen compounds in water

Enrichment: (preliminary separation)	Liquid-liquid extraction discontinuous continuous (stages)
	Blowing out static (headspace) dynamic (concentration)
	Adsorption (elution) batch test column
Separation:	Gas chromatography packed columns capillary columns
Determination:	Mass spectrometer Conductivity detector Microcoulometer Electron capture detector (ECD) Plasma detector Neutron activation Pyrohydrolysis (+ chloride determination)

As shown in the next table, the enrichment can be divided into the following steps:

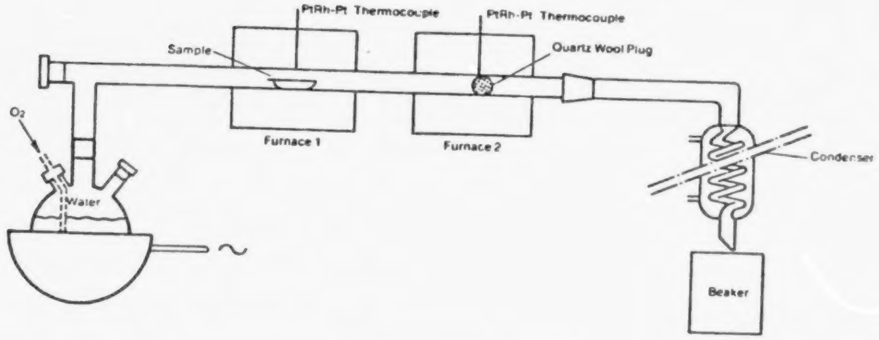
TABLE 2 Experimental conditions of the combination of adsorption and flocculation for TOCl treatment

ADSORPTION:	solution	: 1-20 litres
	pH	: ≤ 3
	powdered carbon	: 100 mg/l ≤ 60 µm
	$NaNO_3$	: 0.01 N
	time	: 30 min
FLOCCULATION:	pH	: 6.5-7
	Al^{3+}	: 5 mg/l
	polymer	: 0.4 mg/l
	time	: ca. 5 min
FILTRATION:	blue-band	: (pressure filter)
WASHING:	$NaNO_3$	: 0.05 N (200 ml)
	time	: 30 min
FILTRATION:	blue-band (pressure filter)	

With this enrichment process practically all organic constituents of the water that can be adsorbed and flocculated are enriched. The water to be analysed is first of all treated with solid sodium nitrate to obtain a 0.01 N nitrate solution. This reduces the undesirable adsorption of chloride. After the addition of the active carbon in powder form, the pH is adjusted to ≤ 3 with sulphuric acid. If the carbon suspension is thoroughly stirred, the adsorption process is as a rule completed in half an hour. Most of the supernatant water can be easily siphoned off from the powdered carbon if the carbon is previously flocculated. The flocculating agent is

5 mg Al^{3+} per litre, added in the form of aluminium sulphate. For the flocculation the water must be adjusted to pH 6.5-7 with sodium carbonate. To assist the flocculation, 0.4 mg/l of partly saponified polyacrylamide is added to the water and is subsequently decanted off. This process can be repeated if a more complete treatment is desired. After filtration of the combined sludges through filter paper, the filter cake is suspended in 200 ml of 0.05 N sodium nitrate and stirred for half an hour. This removes nearly all inorganic chloride.

The filter cake is then subjected to pyrohydrolysis, the organically bound chlorine being thus converted into inorganic chloride, as is shown in the following diagram.



Pyrohydrolysis Apparatus

Fig.1

This mineralization takes place in a current of steam and oxygen at 900°C in a tubular furnace. The chloride is then determined titrimetrically or microcoulometrically.

By means of this pyrohydrolysis technique, the organic chlorine materials can be treated as a group. As preliminary individual investigations have shown, the majority of the polar compounds are high-molecular, chlorinated lignic and humic acids.

In order to investigate on a laboratory scale all the processes taking place during the chlorination of water, model waters containing humic acid were treated with chlorine water, since humic acid can be used as a starting substance for haloforms. An example of the results of this work is given in the following figure.

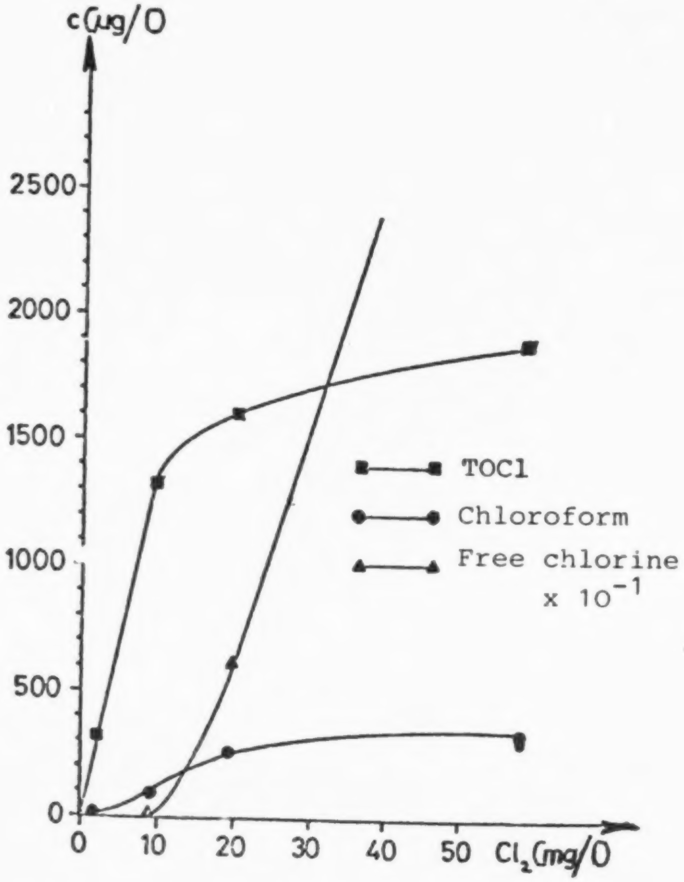


Fig. 2 Chloroform formation, course of TOCl and final chlorine content as a function of the initial chlorine content at a constant reaction time of 23 h

Here the concentrations of chloroform and TOCl are plotted together with the chlorine content in dependence on the dose of chlorine; the amount of humic acid weighed in was 20 mg/l and the pH was 6.9. It is clear that the chlorine content of the chloroform corresponds only to a small part of the total organically bound chlorine. Therefore, the effect of a chlorination cannot be evaluated solely on the basis of the measured haloform concentrations; the TOCl must likewise be considered (6).

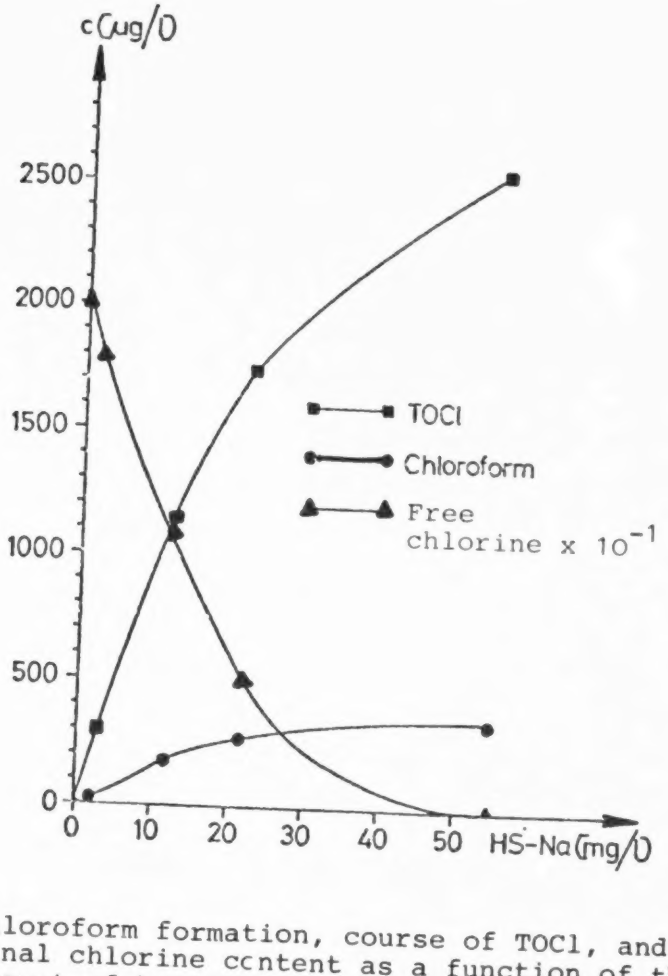


Fig. 3 Chloroform formation, course of TOCl, and final chlorine content as a function of the amount of humic acid weighed in, with a constant reaction time of 23 h

As can be seen from Fig. 3, at a constant amount of chlorine and increasing humic acid concentration, similar relationships are obtained for the formation of organic chlorine compounds.

To obtain information on further parameters influencing the formation of chlorine compounds, in addition to varying the reaction time, we varied the amount of chlorine, the initial humic acid concentration, and the pH. The relationships represented in the following illustration were obtained.

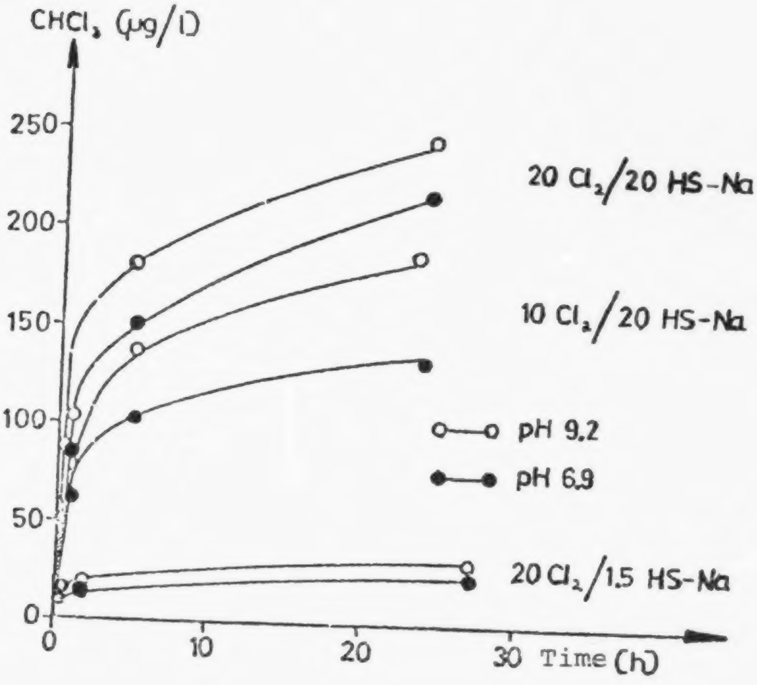


Fig. 4 Chloroform concentrations as a function of the reaction time with various starting conditions (numerical data in mg/l)

In agreement with the relationships reported in the previous lecture by Dr. Stevens, more chloroform is produced at pH 9.2 than in the neutral range.

In contrast to this, the formation of TOCl is enhanced at lower pH, as shown in the next figure.

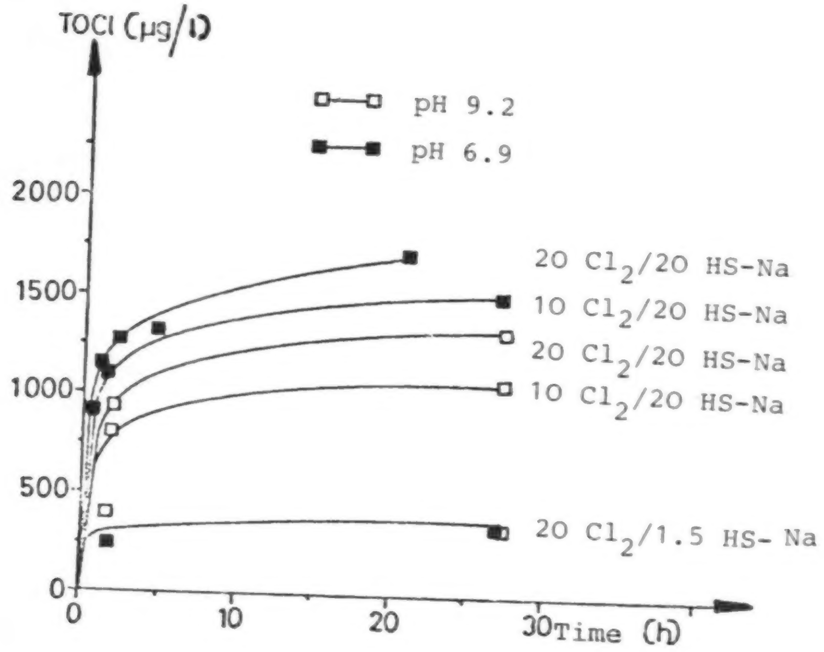


Fig. 5 TOCl as a function of the reaction time with various starting conditions (numerical data in mg/l)

In the experiments performed here, the haloform reaction ended after about 24 h.

At pH 6.9 there was a clear increase in the amount of TOCl formed. The influence of the pH on the chlorine consumption or the TOCl formation can be explained by the increase in the electrophilic character of hypochlorous acid in the acid medium.

In addition to these relationships, it was also of interest how the formation of the organic chlorine substances is influenced by suitable pre-treatment methods (7). Since ozonization is regarded in waterworks operation as a practical possible solution, further experiments were performed after a preliminary ozonization. The results on the formation of polar and higher-molecular halogen compounds after ozonization, measured as TOCl, are shown in the next illustration.

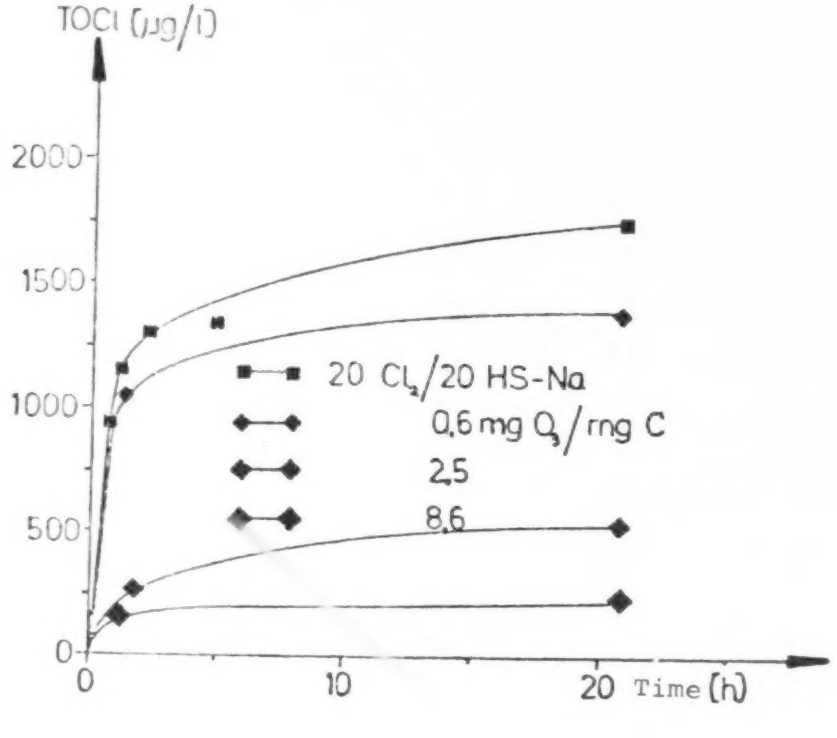


Fig. 6 Course of TOCl as a function of the reaction time with various ozone consumptions (20 mg/l chlorine + 20 mg/l HS-Na)

The diagram demonstrates that even small additions of ozone noticeably reduce the formation of organic chlorine compounds. In the present case an ozone addition of 2.5 mg/l water reduces the TOCl formation to one-quarter of that formed in the absence of ozone.

Similar results were obtained for chloroform formation, as shown in Fig. 7.

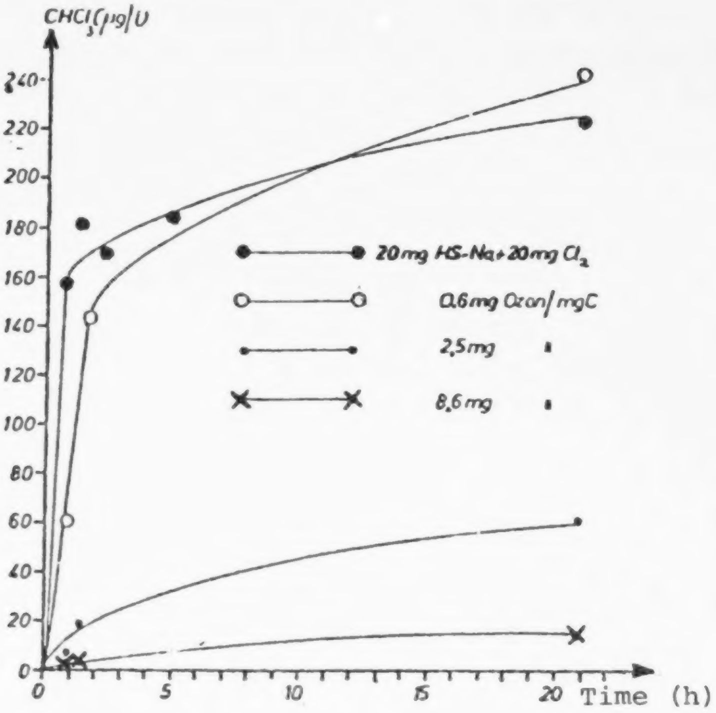


Fig. 7 Chloroform formation as a function of the reaction time with various ozone consumptions (20 mg/l of chlorine + 20 mg/l HS-Na)

In this respect, however, different authors have obtained different results.

In practical water-works operation other effects on the formation and behaviour of the organochlorine compounds are of interest. Chlorine is used in large quantities especially for the removal of ammonia in so-called break-point chlorination. For this reason the TOCl formation in the presence of ammonia was studied. The results are summarized in Fig. 8.

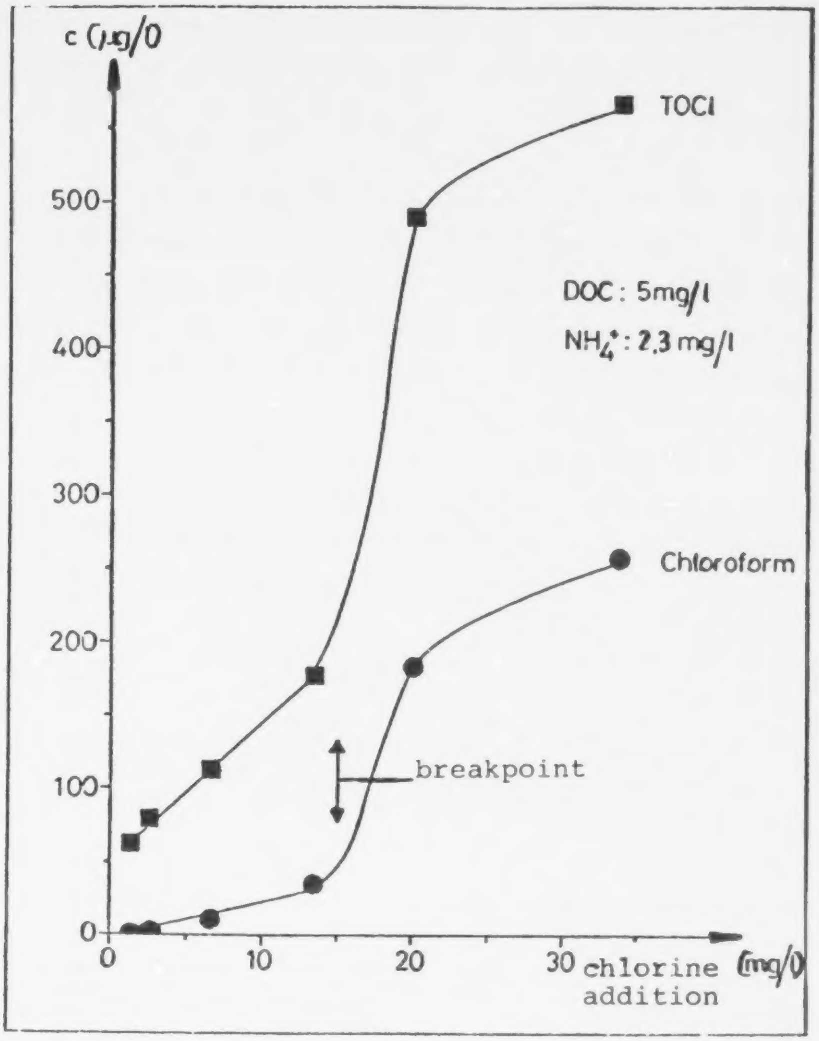


Fig. 8 Chloroform and TOCl concentrations as a function of the initial chlorine concentration after a reaction time of 20 h

It can be seen clearly that below the break-point, where for a short time until the formation of chloramines still relatively little free chlorine is present, the formation of chloroform and of TOCl is very low.

After the break-point has been reached, however, a small addition of chlorine is sufficient to form large amounts of these constituents.

These results are in accord with trials in an experimental plant in Stuttgart municipal works, where good results were obtained with stepwise chlorination just up to the break-point. In comparison with the conventional practice, this reduced the formation of chlorine compounds by a factor of 10.

The data on the conventional procedure, obtained from the same experimental plant, are compiled in Table 3.

TABLE 3 Effects of classical treatment for a river water (Neckar, Stuttgart) with break-point chlorination and activated carbon filters

	River water	After breakpoint chlorination, flocculation, sedimentation and filtration	After GAC Carbon LSS	After GAC Carbon F 300
Dissolved organic carbon (DOC) mg/l	5.0	4.1	3.1	1.6
UV absorbance at 254 nm m^{-1}	10.9	8.6	5.0	3.6
Sum of haloforms µg/l	0.4	50	16	25
Total organic chlorine (TOCl) µg/l	33	524	364	296

After chlorination with 20 mg of chlorine per litre, both the haloform concentration and the TOCl concentration rise sharply. The quantity of trihalomethanes accounts for only 10% of the total chlorine compounds formed. This large proportion of polar chlorine compounds, which essentially still resist individual analysis, is serious, especially in view of the fact that, as can be seen from the last two columns of the table, these compounds are also adsorbed only with difficulty in the subsequent active carbon filter (8). A selectivity of the active carbon filters is evident, since the carbon, which removes the TOCl less efficiently, adsorbs the trihalomethanes better and vice-versa.

These statements are confirmed by measurements made in a water treatment plant at the Rhine. The results are collected in the following table.

TABLE 4 Course of the concentration of trihalomethanes and of the total organically bound chlorines during the treatment of drinking water in a Rhine waterworks

	$CHCl_3$ x)	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	Σ THM	TO Cl
River bank filtrate	2,3	n.n.	n.n.	n.n.	2,3	35
Raw water after chlorination (2 mg Cl_2/l)	7,3	16,5	15,5	3,0	42,3	--
After filtration	5,1	10,7	11,1	2,4	29,3	195
After active carbon filter	0,9	1,0	0,6	0,2	2,7	55

x) All data in mg/m^3 n.n. = no trace

Here too, large amounts of organic chlorine compounds other than the haloforms are produced in chlorination with 2 mg Cl_2/l. However, the variation of the concentration of these compounds in the course of the treatment is interesting. The chloroform, which in comparison with the other trihalomethanes is more soluble in water, is also less efficiently removed by adsorption in the active carbon filter, but in general the total amount of haloforms is better removed by adsorption than the polar organic chlorine compounds here grouped as TOCl. The difficulty that these substances also present from the point of view of treatment technology, means that greater attention should be paid to them in water quality control.

Summing up, it can be said that, in addition to the trihalomethanes, far greater amounts of high-molecular chlorine compounds can be produced. The compounds that can be determined by individual substance analysis represent only the tip of the iceberg. The aim of further research must be to learn more about the structure of these polar compounds and about their formation reactions.

(1) KÜHN, W., SANDER, R.
Vorkommen und Bestimmung leichtflüchtiger Chlorkohlenwasserstoffe
Hydrochem. hydrogeol. Mitt. 3 (1978), 327-340

(2) STIEGLITZ, L., ROTH, W., KÜHN, W., LEGER, W.
Das Verhalten von Organohalogenverbindungen bei der Trinkwasseraufbereitung
Vom Wasser 47 (1967), 347-377

(3) KÜHN, W., SONTHEIMER, H.
Zur analytischen Erfassung organischer Chlorverbindungen mit der temperaturprogrammierten Pyrohydrolyse
Vom Wasser 43 (1974), 327-341

(4) KÜHN, W.
Untersuchungen zur Bestimmung von organischen Chlorverbindungen auf Aktivkohle
Dissertation, Universität Karlsruhe (1974)

(5) KÜHN, W., FUCHS, F., SONTHEIMER, H.
Untersuchungen zur Bestimmung des organisch gebundenen Chlors mit Hilfe eines neuartigen Anreicherungsverfahrens
Z. f. Wasser- und Abwasser-Forschung 6 (1977), 192-194

(6) SANDER, R., KÜHN, W., SONTHEIMER, H.
Untersuchungen zur Umsetzung von Chlor mit Huminsubstanzen
Z. f. Wasser- und Abwasser-Forschung 5 (1977), 155-160

(7) KÜHN, W. et al.
Use of ozone and chlorine in water utilities in the Federal Republic of Germany
J. AWWA, June (1978), 326-331

(8) KÜHN, W., FUCHS, F.
Untersuchungen zur Bedeutung der organischen Chlorverbindungen und ihrer Adsorbierbarkeit
Vom Wasser 45 (1975), 217-232

REDUCTION OF THE CONTENT OF CHLORINE COMPOUNDS BY A TREATMENT COMBINING PHYSICO-CHEMICAL AND BIOLOGICAL PROCESSES

J. Chedal and P. Schulhof

INTRODUCTION

The waterworks which supply Paris with drinking water, and notably the largest one, all treat surface water.

These plants were built about twenty years ago, following the classical pattern of physico-chemical treatment:

- chemical pre-treatment comprising oxidizing agents, in this case chlorine and chlorine dioxide, and an adsorbing agent: powdered activated carbon;
- coagulation;
- flocculation, decantation, rapid sand filtration;
- final addition of chlorine before injection into the distribution network.

Several years later a further treatment was added: ozonization of the filtered water with a residual content of 0.4 mg/l maintained for over 10 minutes. Lastly, treatment aimed at protecting the distribution network was instituted by means of a combined treatment with chlorine and chlorine dioxide.

Precautions were taken at each stage of the plant construction to ensure that the process could be adapted as time went by with a minimum of labour, to keep pace with technical advances, degree of river pollution, and quality objectives for the treated water.

Today these precautions have proved very valuable, for many changes have taken place in the course of the last twenty years.

In the first place, the pollution of the Seine has greatly increased. Although the water to be treated is collected upstream of Paris, the built-up area has spread and there has been a great deal of urban growth upstream of the water-collection point. The water has become increasingly charged with ammonia (see Fig. 1).

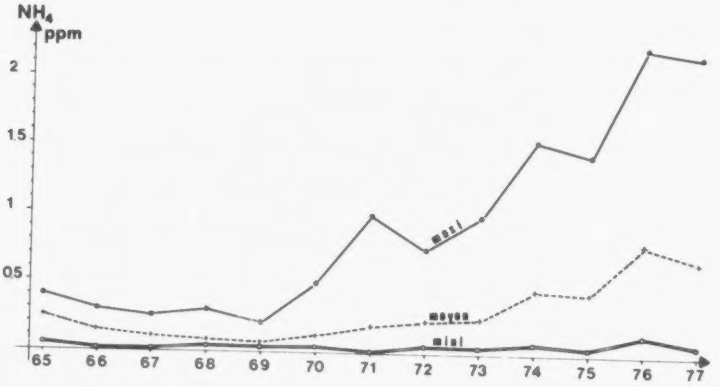


Fig. 1 Content of ammonia in Seine water

It is above all extremely rich in organic matter. During the second half of 1977, for example, the mean amount of non-volatile organic carbon was greater than 5 mg/l, with a maximum of 9.6 and a minimum of 2.8. On the other hand, the water contains a relatively small amount of organo-chlorine compounds and trihalomethanes. In the course of 1977, for example, the amount of chloroform varied between 0 and 28 µg/l, with a mean content of 6.5 µg/l.

In parallel with this, during the last twenty years the requirements on the quality of the treated water have developed in a way that we all know.

In connection with this development, one of the first objectives to reach is discontinuation of the pre-treatment with chlorine at the breakpoint. This is a process that certainly eliminates ammonia, but it also leads to the formation of a substantial amount of haloforms.

Another objective is to obtain treated water containing a minimum of organic substances.

DESCRIPTION OF THE TESTS

A pilot plant was built to test the efficiency of the various improvements. It comprises two lines of treatment, each capable of processing 10 m^3/h, and in which the stages of pre-treatment, flocculation, decantation, filtration, and ozonization are exactly the same as those in the full-size plant (Figs. 2-4).

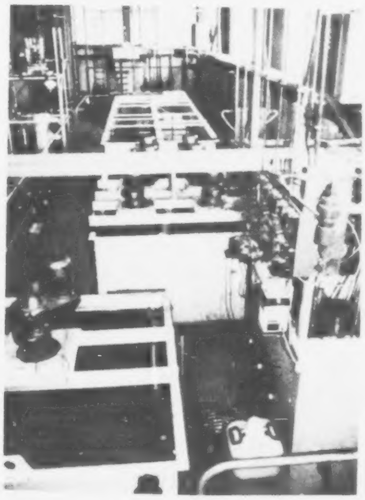


Fig. 2
Flocculation and
decantation units
in the pilot plant

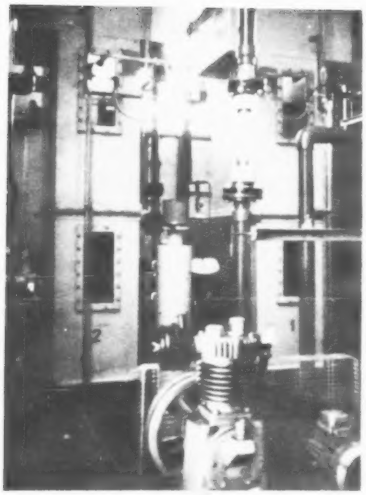


Fig. 3

Filters of the pilot plant

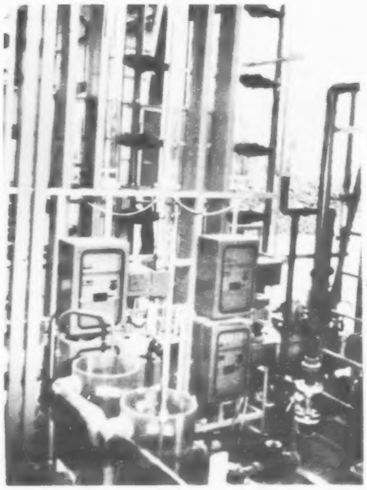


Fig. 4

Post-ozonization columns in the pilot plant

During the various tests undertaken one line was equipped for specific treatments, consisting of modifications or additions as compared with the reference line. This enabled the effects of these modifications on the water quality at all the different stages to be determined.

The aim of the tests, whose results are reported below, was to examine the effects of two modifications:

- preliminary ozonization of the raw water as an oxidation process before coagulation and, in conjunction with this, discontinuation of the chlorine pre-treatment;

- filtration through activated carbon instead of sand.

Several of the filters, with a specific surface of 117 m^2, were filled with activated carbon. The qualities of carbon and the gradings most suitable for satisfactory filtration were subsequently tested, and the optimum treatment parameters were determined. It was found, in this respect, that the life of the activated carbon filters between two treatments was longer than that of sand filters. We were also able to verify, as others have done before us, the rapid disappearance of the adsorptive properties of the carbon, except in matters of flavour. However, during these tests in the full-scale plant, chlorine-oxidized water was passed through the filters. It was therefore interesting to judge the effect of a carbon filter on water oxidized by ozone used in pre-ozonization.

Consequently, the following general scheme wad adopted in the pilot tests (see Fig. 5):

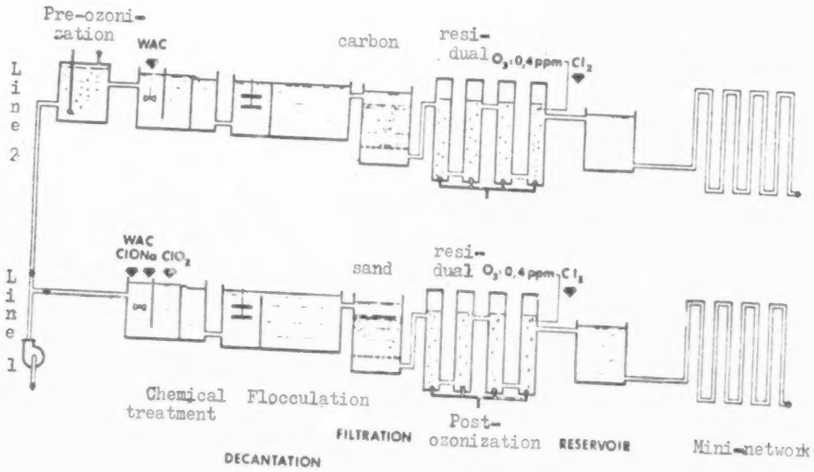


Fig. 5 General scheme of the experimental lines

- In the control line (ref. No. 1) the treatment corresponds to that in the plant, whose characteristics are as follows:

1) At the pre-treatment stage: chlorination at the breakpoint with Javel water;

   addition of chlorine dioxide to eliminate phenols, manganese, and certain flavours;

   coagulation by means of poly-aluminium chloride.

2) After the 0.4 g/m^3 residual post-ozonization treatment: post-chlorination.

- In the experimental line (ref. No. 2), the treatments differ from the control line as follows:

  pre-ozonization carried out with semi-industrial emulsifier-type equipment. The total contact time is about 2 min, but the characteristic feature of the treatment is the time of contact of a bubble of ozonized air with the water, which is about 20 sec.

  Omission of the chlorine pre-treatment.

  Filtration through activated carbon instead of filtration through sand as used in the control line.

The purpose of the experimental scheme for this line was to favour bacterial development: oxygenation of the raw water, omission of the chlorine pre-treatment, and suitable filtration material. In the rest of this report, this will be known as the biological scheme.

The tests were conducted with a view to determining the effects of the pre-ozonization conditions on the quality of the water at different stages of treatment. Consequently, the following operations were carried out during the essential phases of the tests:

1. Operation for several months with constant pre-ozonization conditions: treatment dose of 0.25 g/m^3 and an air concentration of 1.5 g of ozone per m^3, or an air/water ratio of 17 %.

2. Operation with pre-ozonization treatment dose varying between 0.20 and 4 g/m^3, but with a constant air/water ratio of about 16 %.

3. Variation of the two characteristics of pre-ozonization, i.e. the treatment dose and the air/water ratio. This phase of the trials is currently in progress, and we can only give the initial results.

During all these experiments the treatments common to both lines were applied under the same conditions. The treatment dose of coagulant was determined by the jar test, and the post-ozonization was chosen with a view to obtaining a residual virulicidal content of 0.4 mg/l after 10 min of contact.

We shall discuss the quality of the water tested at different stages of treatment during the various phases outlined above.

EFFECT OF PRE-OZONIZATION ON RAW WATER

As regards the raw water, the results obtained over a period of three months (trial with pre-ozonization at a constant strength of 0.25 ppm) enable us to draw the following basic conclusions (see Fig. 6).

The pre-ozonized water is richer in suspended matter, it is more turbid and more clogging. This development is due to the decomplexing and coagulating properties of ozone.

Pre-ozonization	Turbidity (drops of mastic)	Suspended matter (mg/l)	Beaudrey clogging power (ℓ^{-1})	N.V.T.O.C. (mg/l)	UV absorption at 250 nm (O.D. 10^{-3} cm^{-1})
Before	400	54	7	7	148
After	430	72	9.4	7	139

Fig. 6 Quality of the raw water before and after pre-ozonization

As regards organic matter, the smaller value of UV absorption in the pre-ozonized line certainly confirms the action of ozone on organic molecules - the total amount of organic matter remains unchanged, as indicated by the values of non-volatile organic carbon.

When the intensity of the pre-ozonization treatment is increased, the difference in UV absorption between the two treatment lines also increases, as long as the pre-ozonization treatment dose does not exceed about 1 mg/l. Beyond this threshold level the difference between the UV absorptions remains essentially constant (see Fig. 7).

This result shows that pre-ozonization does not eliminate organic matter but modifies their structure. This action increases with increasing doses of ozone until about 1 mg/l is reached.

The results obtained with an air/water ratio of 16 % for the pre-ozonization seem to be fairly analogous regardless of the air/water ratio, as shown by the first results of the most recent tests still in progress.

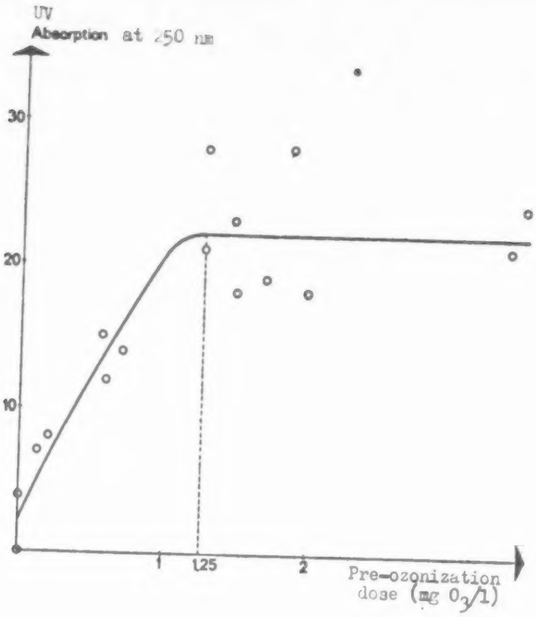


Fig. 7

Reduction of UV absorption as a function of the pre-ozonization dose

The amount of oxygen dissolved in the water increases significantly as a result of pre-ozonization. During the last tests, carried out in August 1978, pre-ozonization enabled the amount of dissolved oxygen to be increased from a saturation level of 75 to 85 % in relation to the atmosphere.

AMMONIA CONTENT IN THE TWO TREATMENT LINES

Ozone has no direct effect on the elimination of ammonia. There is therefore no difference between the ammonia concentrations in pre-ozonized raw water and initial raw water.

At the stage where the water is decanted, the experimental results show that after a period of one month there is a very marked reduction of the ammonia level in the pre-ozonized line. The values obtained are of the same order as those in the control line, in which the breakpoint pretreatment was kept up during the first five months of the tests (see Fig. 8).

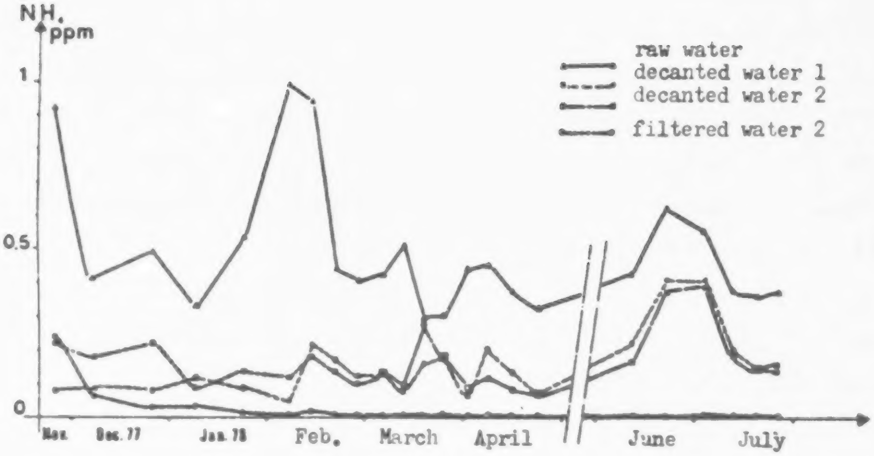


Fig. 8 Ammonia contents

In the pre-ozonized line biological elimination took place in the layer of sludge formed in the flocculators.

During the subsequent filtration the same test shows that the ammonia remaining after decantation is easily eliminated. A delay in inoculation was, however, necessary for the new activated carbon introduced into the filter.

Nitrification seems to occur principally in the upper layer of the filter, as evidenced by the counts of nitrite and nitrate germs at different depths.

From the beginning of June 1978 the treatment at the breakpoint was discontinued in the control line. It was ascertained (see Fig. 8) that nitrification was just as effective in the decantation unit without pre-ozonization. Under these conditions, this treatment contributed nothing to the biological elimination of ammonia.

For the amounts of ammonia of the order of 2 ppm that can be encountered in the river, the dissolved oxygen will, however, be insufficient. Pre-ozonization then will provide enough oxygen to bring about nitrification.

Thus, although pre-ozonization has no direct effect on the elimination of ammonia, it does seem to be useful in this respect for bringing about biological nitrification when the amount of ammonia present exceeds a certain limit. However, the essential advantage of replacing chlorine by ozone in the pre-oxidation is that no halogenated compounds are formed during the pre-treatment.

The content of chloroform in the treated water after the final protective chlorination treatment was markedly smaller in the biological line (Fig. 9). This infers a significant elimination of precursors by a biological route.

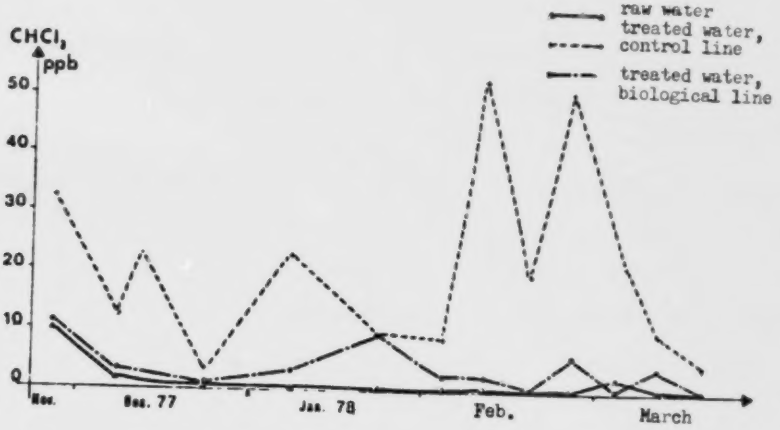
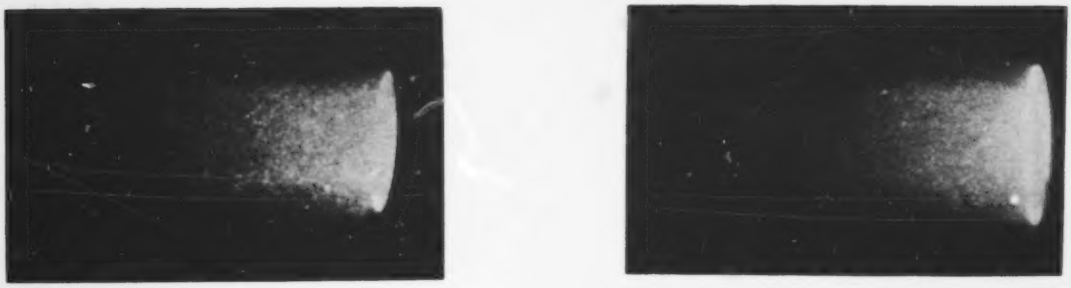


Fig. 9 Chloroform content

ELIMINATION OF ORGANIC MATTER FROM DECANTED WATER

The effect of pre-ozonization in the pre-treatment on coagulation - flocculation - is very marked. The flocculate in the treatment line, where pre-ozonization had been used, was far coarser, as can be seen from Fig. 10.



Flocculate in the
pre-ozonized line

Flocculate in the
non-preozonized line

Fig. 10

The effects of the pre-ozonization can be noticed from a dose of about 0.2 ppm onwards. Pre-ozonization is therefore more effective as an oxidizing pre-treatment for coagulation than is pre-chlorination. This advantage indicates an improved elimination of the organic matter in the line with pre-ozonization.

What is the situation with respect to the organic carbon parameter? The results obtained with UV absorption of the raw water have shown that it might be useful to proceed to pre-ozonization with relatively high doses (about 1 ppm). This supposition was confirmed for the decanted water, where it had been found that the difference between the organic carbon contents in the two treatment lines increases in favour of the biological line, with an increasing pre-ozonization dose of up to about 0.6 mg/l (cf. Fig. 11). Above this dose the difference between the organic carbon contents is 0.7 ppm.

When the treatment at breakpoint in the control line is discontinued, it seems that this difference is not altered to any significant degree. The results obtained so far indicate a mean difference of 0.6 ppm.

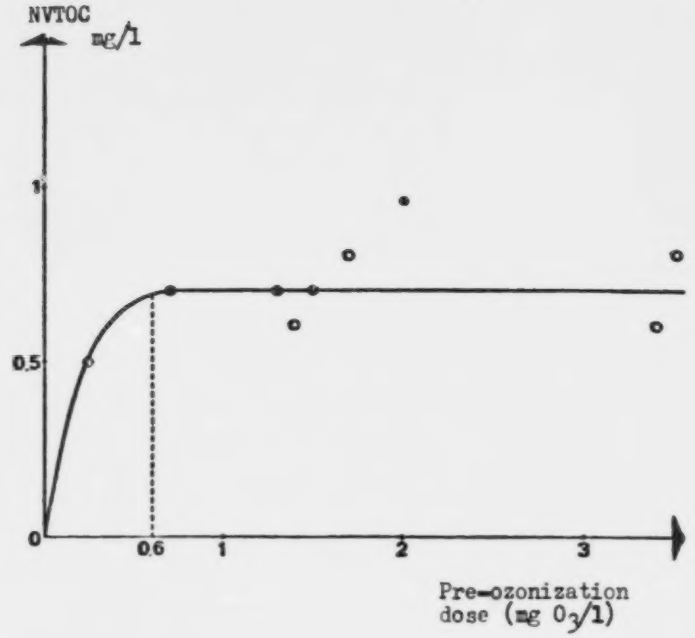


Fig. 11 Reduction of the content of non-volatile organic carbon in decanted water as a function of pre-ozonization dose

Thus, pre-ozonization is certainly the reason for the better results obtained with decanted water in the biological line.

ELIMINATION OF ORGANIC MATTER IN THE FILTERED WATER

The first measurements in filtered water showed very low contents of organic carbon in the biological line. This was in no way due to the biological activity of the filter, but to adsorption on the activated carbon, which had only just been placed in the filter.

At the end of several months of operation at the rate of 4 volumes per hour the findings corroborated earlier experience and the results reported by many other investigators: the effects of adsorption are then very much reduced and essentially constant. Any improvements observed in the filtered water are thus a result of biological activity.

The measurements taken in the course of the test with varying pre-ozonization doses show differences between the organic carbon contents in the two lines which are much the same for the filtered water and for the decanted water.

However, the results obtained are certainly not wholly incontestable. Thus, the time after every change in the pre-ozonization conditions, about a week, was perhaps too short to have allowed the bacterial population of the filter to adapt itself to each new situation.

In order to evaluate the biological activity of the filter with respect to organic matter, we also measured the content of detergents, compounds that are easily biodegradable. The results obtained show that during filtration through activated carbon this parameter was only reduced to about 70 % (cf. Fig. 12).

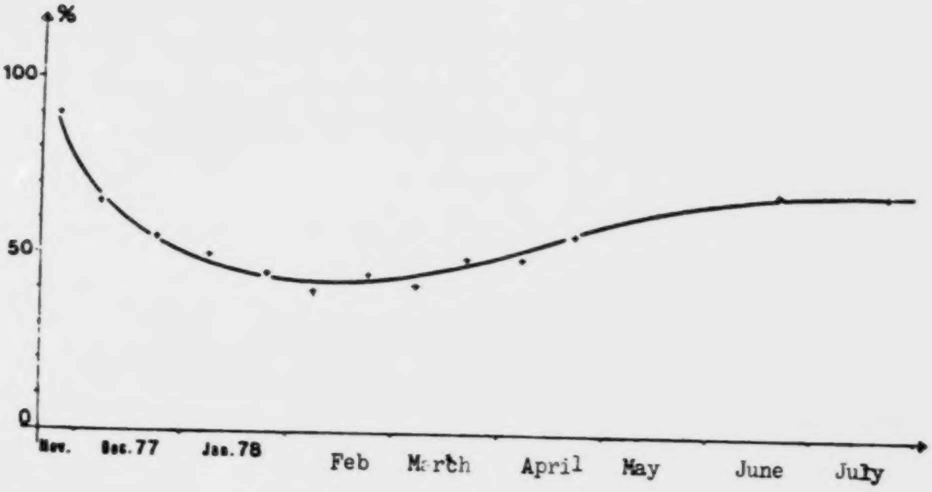


Fig. 12 Reduction of the amount of detergent by filtration through carbon (biological line)

It is interesting to compare this finding with those obtained in a test on filtration through carbon, carried out with filtered and ozonized water produced in a large plant. It was noted at the time that the amount of detergents was totally and constantly reduced, even though the water had been pre-treated at the breakpoint. However, this total elimination was obtained only when the flow rate had been reduced to 12 m/h, which corresponded to 4 volumes per hour (see Fig. 13).

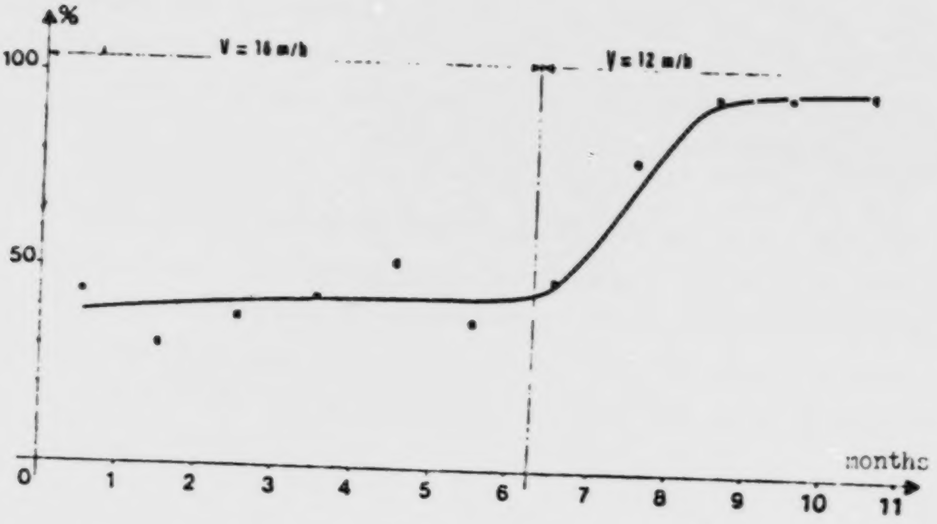


Fig. 13 Reduction of the amount of detergents by secondary filtration after post-ozonization

Subject to the speed of filtration through activated carbon not being too great, these results lead us to the conclusion that far more efficient biological activity as regards organic matter can be obtained on a filter after secondary ozonization (ozonization after complete clarification) than on a filter placed in first filtration, even preceded by pre-ozonization. It is highly probable that the lower biological yield with respect to organic materials observed with the latter type of filter is due to the periodical washing to which the filter is subjected.

We are therefore continuing with the pilot tests, studying the efficiency of filtration after secondary ozonization to complete the elimination of organic substances already achieved in the biological line that we have been testing. The initial results of these trials have been fairly encouraging.

EFFECT OF PRE-OZONIZATION ON VIRULICIDAL POST-OZONIZATION

Another very important action of pre-ozonization is the effect that it has on the behaviour of water during post-ozonization. This treatment was tried out in a pilot line with a view to obtaining a residual virulicidal content of 0.4 g/m^3 in the water for a time of 10 min.

It was found that, in order to arrive at this result, the treatment doses required should be 40 % to 50 % lower in the biological line than in the chemical line. This saving on ozone in post-treatment remains fairly constant for all pre-ozonizations above 0.25 ppm (cf. Fig. 14).

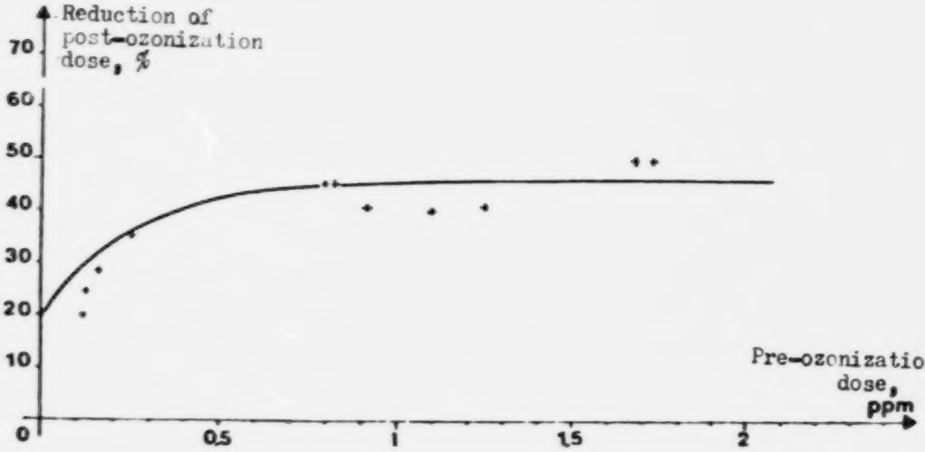


Fig. 14 Reduction of the post-ozonization treatment dose as a function of the pre-ozonization dose

Since the mean post-ozonization dose in the treatment of Seine water is 2.5 ppm, the application of pre-ozonization at 1 ppm will not necessitate the installation of supplementary ozone-generation equipment. All that will be required for pre-ozonization is a different distribution of the existing production. Thus, pre-ozonization can be considered to be "gratis".

PEHAVIOUR OF TREATED WATER IN THE DISTRIBUTION NETWORK

To compete the appraisal of the treatment lines tested, the pilot line was equipped with two mini-networks made of unlined cast-iron pipes 100 mm in diameter. The water moved very slowly in these pipes, to obtain a residence time of 4 days (see Fig. 15). Sampling points were provided to allow the water to be collected after residence times of 1, 2, 3 and 4 days.

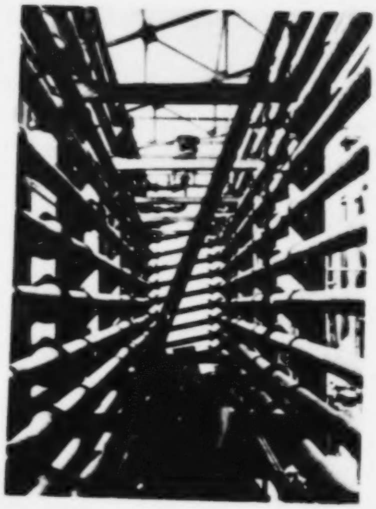


Fig. 15

Mini-network in the pilot plant

The counts of the banal bacteria present in these samples enabled the risk of bacterial re-growth in the water produced to be calculated. The figures obtained for the water produced in the tests show that in the biological line the maximum count reached was about 200 bacteria/ml, and in the control line only 150/ml. This difference is of little significance, and it can be assumed that bacterial re-growth will be identical for the two types of water (cf. Fig. 16).

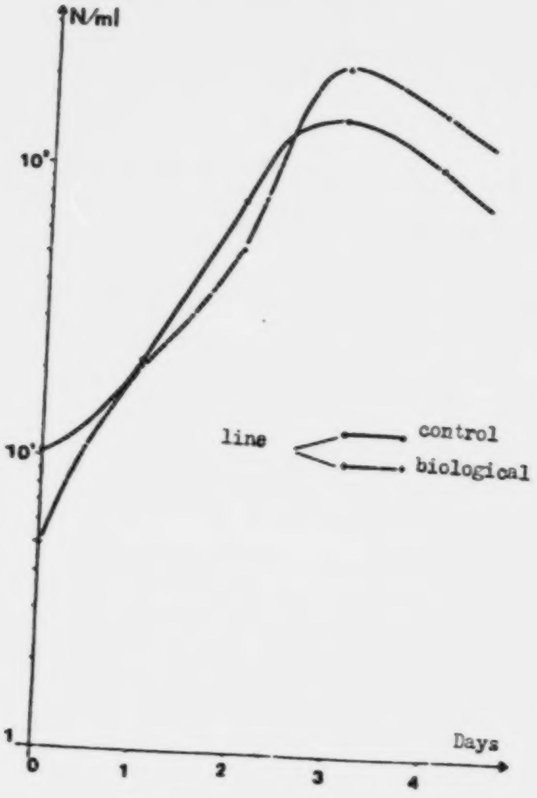


Fig. 16

Banal bacteria counts in the mini-network

CONCLUSION

The results of the tests indicate that the pre-ozonization treatment of Seine water before coagulation presents many advantages over the chlorine pre-oxidation practised so far.

- It enables the pre-chlorination treatment at the breakpoint to be discontinued, for it constitutes the first link of a chain in which ammonia is eliminated in a biological way.

This solution to the problem entails a reduction of the amount of organochlorine compounds in the water produced, and in particular of haloforms, this being due to the elimination of precursors in the course of the biological clarification process.

- Pre-ozonization leads to an appreciable improvement in the elimination of organic matter, essentially in the decantation units.

It does not appear, however, that this improved elimination occurs by the biological route during filtration through activated carbon.
The use of a second filtration after secondary ozonization is undoubtedly necessary to obtain a complementary increase of elimination of organic substances by a biological route.

- Lastly, it must be pointed out that pre-ozonization does not entail any supplementary use of ozone, bearing in mind the economies that such treatment would bring to post-ozonization.

PHYSICAL-CHEMICAL PRETREATMENT FOR THE REMOVAL OF PRECURSORS

J.M. Symons and A.A. Stevens

INTRODUCTION

The reaction of chlorine and precursors to yield chlorinated organics, as represented by Figure 1, would indicate three possible ways exist to attack the trihalomethane problem: 1) is the removal of the precursors by some treatment technique; 2) is to replace chlorine with some alternate disinfectant, or 3) is to remove the chlorinated organics once they are formed. This paper will review what is known about removal of precursor as a trihalomethane control procedure. Discussion of the other two techniques can be found elsewhere (1,2,3).

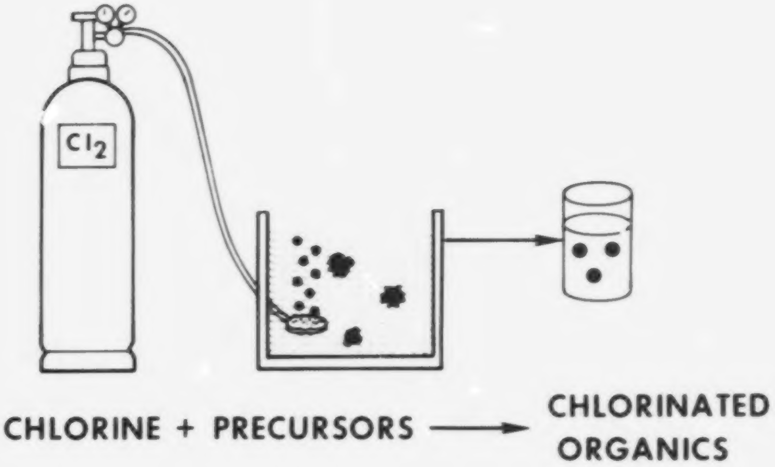


Fig. 1

REMOVAL OF PRECURSORS

For removal of precursors, three possible techniques have been explored: precipitation, oxidation, and adsorption, precipitation being either during lime softening or during turbidity and color removal with a coagulant, oxidation either with ozone, chlorine dioxide, or potassium permanganate, and adsorption either with powdered or granular activated carbon.

Precipitation

Pilot plant data would indicate that the amount of chloroform that is formed during treatment can be changed depending on the point of application of the chlorine (see Figure 2), either ahead of the flocculation basin, ahead of the filter, or after filtration. This

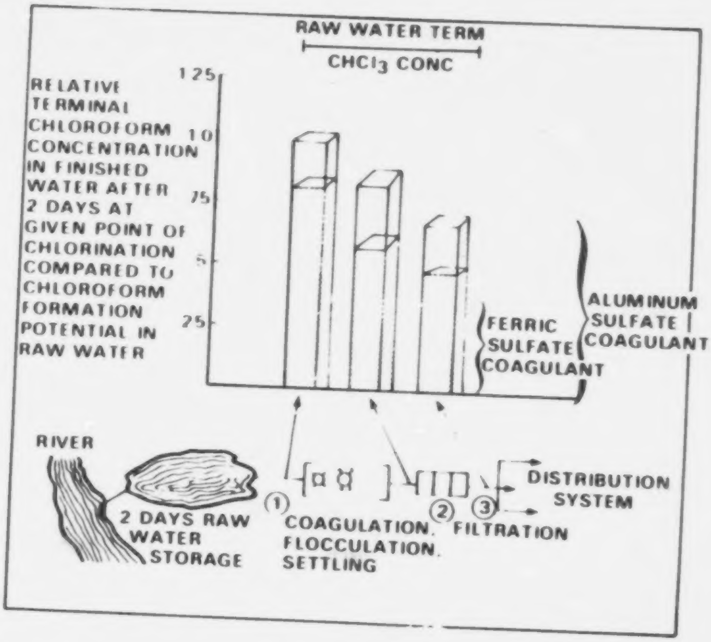


Fig. 2 Chloroform in finished water relative to point of chlorination (pilot plant studies)

indicates that precursors are being removed during treatment, and the later in treatment that chlorine is applied, the less chloroform is produced. In this particular water from the Ohio River, ferric sulfate was a more effective coagulant and so the solid part of the bars in Figure 2 indicates the ferric sulfate data, the total bar the aluminium sulfate data.

Raw water data are also indicated in Figure 2 for the terminal trihalomethane concentration and a question frequently arises as to why the raw water terminal trihalomethane concentration is higher than the amount of trihalomethane produced when raw water is chlorinated in a treatment plant. The explanation is that determination of terminal trihalomethanes is a test that is done in a bottle in which raw water and chlorine are mixed and held for some time and the resultant trihalomethane measured. In the treatment plant the chlorine is added, and as the water is passing through the coagulation and sedimentation basin the precursor and the chlorine are being separated by the settling process. Less trihalomethane is produced under these conditions than would be produced if the raw water was chlorinated in a bottle with precursors and chlorine in contact for the duration of the holding period. Therefore, the raw water terminal trihalomethane is used to indicate the potential in the water, but this potential is not realized even when the raw water is chlorinated during treatment.

Precursor removal by coagulation and settling was first (1975) demonstrated on a full scale at Cincinnati,Ohio, U.S.A. Figure 3 is a diagram of the Cincinnati Water Works. Formerly they added chlorine at point A, where chlorine and coagulant were both added. Then they moved the point of chlorination from point A to point B, the head end of the treatment plant. Because alum was added before presettling (point A), some particulate removal occurred in these basins so the water quality at point B is considerably better than it would be at point A. The results of this change of chlorination practice are shown in Figure 4. After the point of application of chlorine was moved from point A to point B, the chloroform level dropped very dramatically.

In order to demonstrate that this was really caused by the moving of the point of application of the chlorine, and not because of a change in the river quality, the raw water trihalomethane formation potential was measured at various times throughout this period to show that precursors still did remain in the raw water. Even though a slight downward trend in concentration may have occurred through the winter months (Figure 4), it was certainly not equivalent to the dramatic drop in chloroform concentration that occurred when the point of chlorination was moved. Note that the brominated compounds did not change nearly as much in concentration on a percentage basis as did the chloroform.

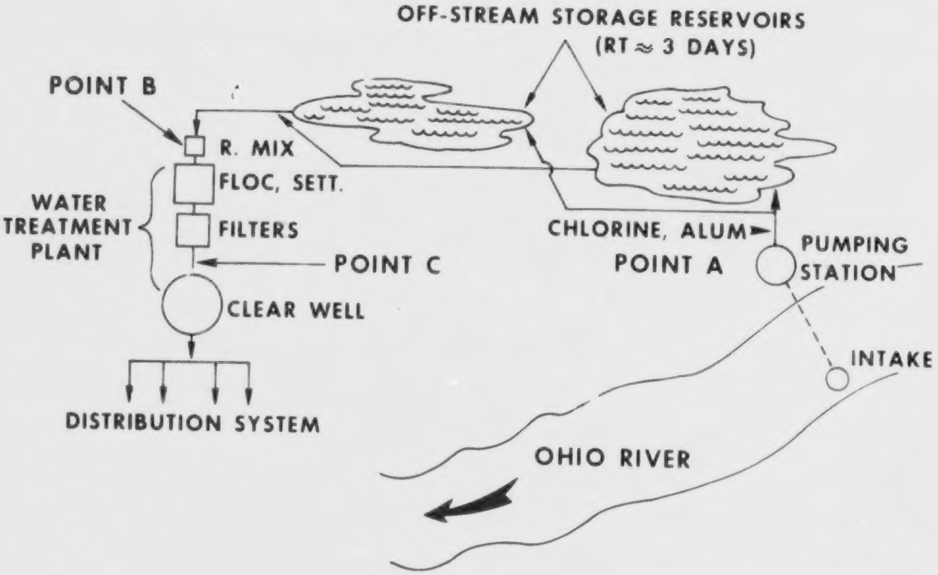


Fig. 3 Schematic of Cincinnati Waterworks

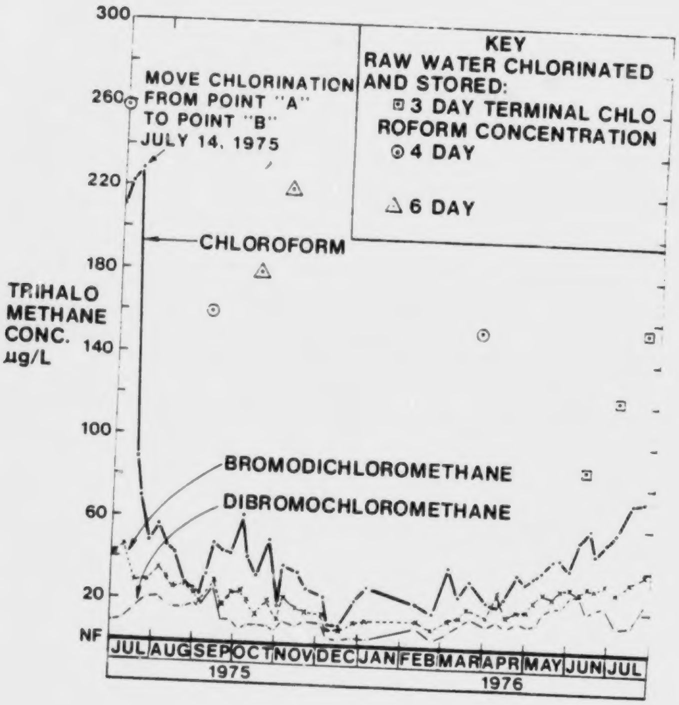


Fig. 4

Trihalomethanes in Cincinnati, Ohio tap water

Another trial was conducted in the late summer of 1977. In this case, the point of application of chlorine was moved from the rapid mix (hydraulic jump) to a point following sedimentation and before the rapid sand filters. Table I shows the trihalomethane concentration in the distributed water for 1976 during mid-September and early October and contrasts these data to those collected during the 1977 study. The generally lower concentrations during the 9/28/77-10/7/77 test again show the advantages of chlorinating as high a quality water as possible.

Figure 5 is a schematic diagram of the Daytona Beach, Florida, U.S.A., treatment plant. This utility did a study in which they chlorinated at three different points, 1) chlorinating the raw water, 2) adding chlorine at the recarbonation basin, and 3) adding chlorine at the clearwell. All of the trihalomethane concentrations were measured at sample point No. 5, which was several hours flow time following the clearwell.

TABLE I INFLUENCE OF MOVING POINT OF APPLICATION OF CHLORINE AT THE CINCINNATI WATERWORKS

Date	Control Year Point of Application of Chlorine	ΣTHM in Distributed Water µg/L	Date	Experimental Year Point of Application of Chlorine	ΣTHM in Distributed Water µg/L
			9/13/77	Rapid Mix	120.8
9/16/76	Rapid Mix	120.1			
21	"	117.5	21	"	107.4
23	"	117.8			
28	"	119.7	28	Settled Water	81.5
29	"	108.9	29	"	102.4
30	"	115.8	30	"	76.0
			10/1	"	89.2
			2	"	87.4
			3	"	116.0
			4	"	78.1
10/5	"	109.7	5	"	77.7
			6	"	77.7
7	"	114.0	7	"	81.0
			10	Rapid Mix	112.9
			11	"	89.9
12	"	92.1			
14	"	109.0			

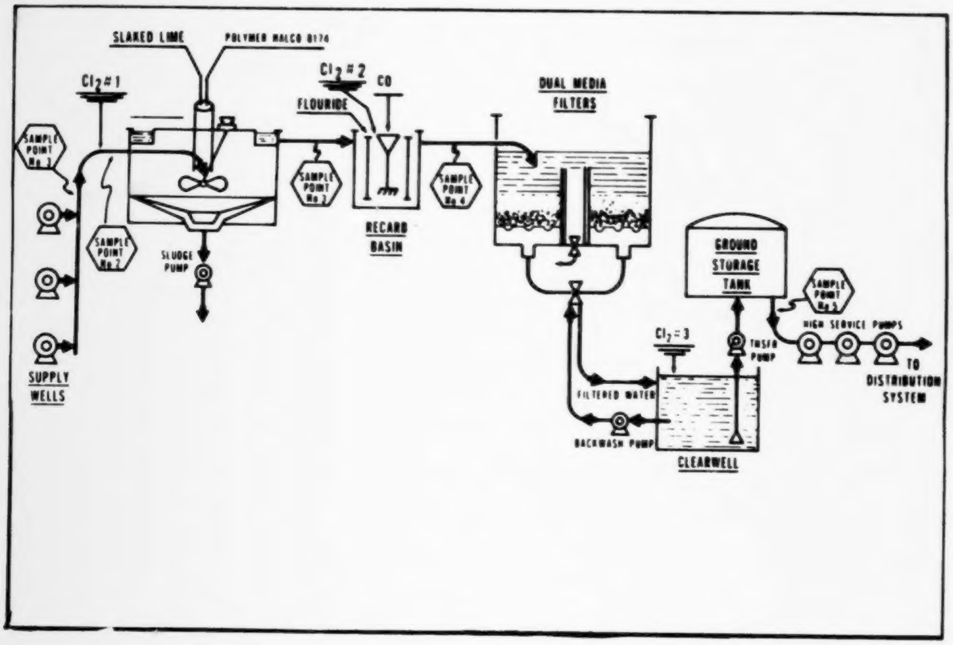


Fig. 5 Flow diagram Ralph F. Brennan Water Plant, Daytona Beach, Florida

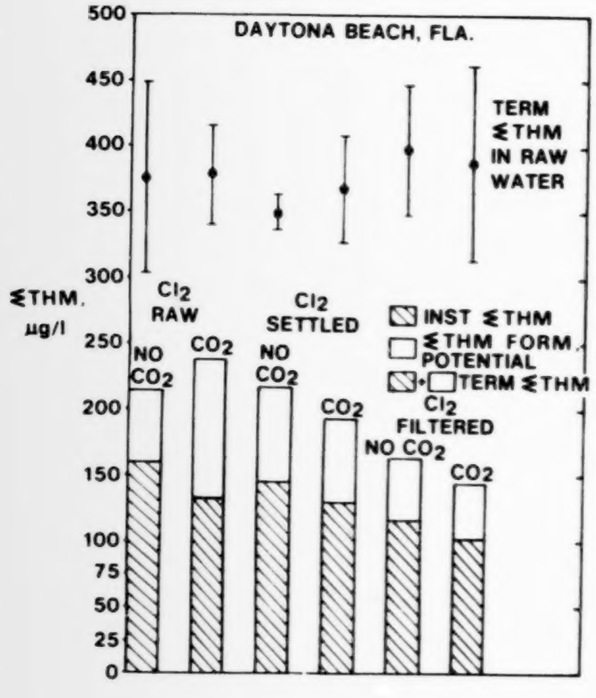


Fig. 6

The first two bars in Figure 6 are weekly average data resulting from chlorinating the raw water; the second pair from chlorination of the settled water; and the third pair from chlorination of the filtered water. The cross-hatched section of the bars shows the instantaneous values that were measured at sample point 5 and the open section additional trihalomethane formation potential that would be exerted out in the distribution system.

The series of studies were conducted both with and without recarbonation, and recarbonation had some effect on the instantaneous trihalomethane concentration because of stripping. In summary, Figure 6 shows two important points: one, the raw water has essentially the same formation potential or precursor concentration throughout the study and, secondly, the benefits of moving the point of application of chlorine are shown. The removal of precursor through coagulation and sedimentation was again demonstrated. The project is continuing in Daytona Beach attempting to demonstrate whether or not this effect can be improved even further through the use of the addition of polyelectrolytes.

Oxidation

- Ozone

Table II shows the effect of ozonation as an oxidant on pilot plant filtered water in Cincinnati, Ohio, U.S.A. Ozone alone does not produce any trihalomethanes. For the first study without ozone and with chlorine, 20 μg/L of trihalomethane was produced. With 0.7 mg/L of ozone plus chlorine, 23 μg/L of trihalomethane was produced. The effect of ozonation was negligible. The same occurred with a dose of 18.6 mg/L of ozone. When a very high dose of ozone was used, 227 mg/L, some oxidation of precursor occurred. Therefore, ozone can be effective in certain circumstances, but in the

Ohio River water it certainly was not particularly effective for precursor oxidation at this time.

Table II EFFECT OF OZONATION OF DUAL MEDIA EFFLUENT

Contact Time - 5-6 min.

Applied O_3 Dose mg/L	Chlorine Dose mg/L	Summation Trihalomethane Conc. after 6 days µg/L
0.7	0	< 0.2
0	8	20
0.7	8	23
18.6	0	< 0.2
0	8	23
18.6	8	30
0	8	123
227	8	70

Figure 7 presents the results of another study performed with Ohio River water during a different time period showing that in this case a big decline in precursor occurred. This study also included an evaluation of the effects of ultraviolet radiation which further enhanced the effects of ozone on removal of precursors. The test system was a 22 liter batch reactor receiving 20 mg of applied ozone per minute. Although this study was also conducted on Ohio River water, the results were quite different from those shown in Table I.

The variability in the observed effect of ozone on trihalomethane precursor removed is further shown by Table III as compiled by Trussel. (4) These data from the independent work of several investigators range from negative removal to 90 percent. Several variables undoubtedly account for the observed wide range of results: nature of precursor, ozone dose, contact time, contactor design, including the dispersion system, and possibly other water quality factors.

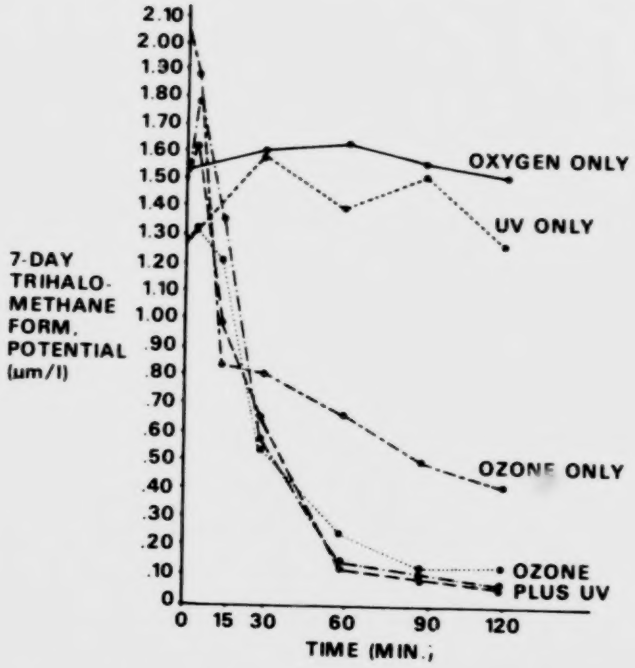


Fig. 7 Ozone and ozone-UV destruction of THM precursors Ohio river water (2/77)

Table III PRECURSOR REDUCTION WITH OZONE x)

Location	Dose, mg/L	% THM Precursor Reduction
Owens River	1.0	78
Lake Casitas	2.0	6
Columbia River	0.5	8
"	1.0	14
"	2.0	16
"	4.0	16
Ohio River	1.0	6
(Louisville)	2.0	22
"	4.0	30
"	6.0	46
"	8.0	46
Bay Bull's Big Pond	1.0	13
	2.0	19
	3.0	27
Ohio River (Cincinnati)	18.6	-31
	227	43
Mokelumne	2.0	62
	3.4	59
	4.5	59
	6.0	53
Middle River	2.6	-13
	2.8	- 3
	5.5	32
	10	7
	11	22
Rotterdam	2	60
	8	50
Orange County	1.0	7
Caddo Lake, Texas	0-72	0-90
Ohio River	0- 109	0-80

x) from R. Trussel, 1978 (4)

- Chlorine Dioxide

The data presented in Figure 8 show some removal of precursor by application of chlorine dioxide. The upper curve is the trihalomethane formation with chlorine alone, the middle curve is similar data with chlorine dioxide and the same amount of chlorine. The chlorine dioxide has some effect on the precursor such that it is changed so that it will not react with the chlorine to form trihalomethanes. The lower curve shows that chlorine dioxide alone does not produce trihalomethanes.

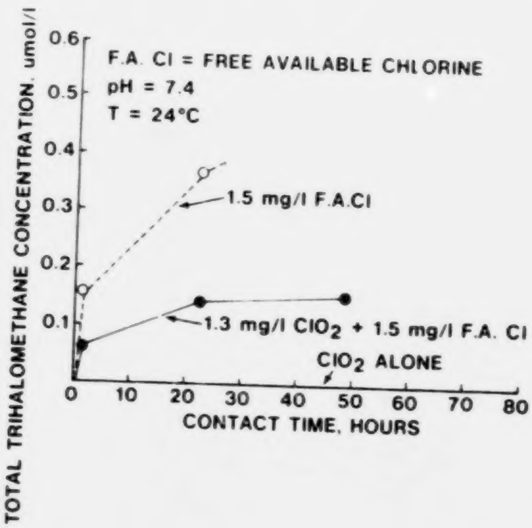


Fig. 8 Trihalomethane formation by ClO_2 and excess free available chlorine, ERC Pilot Plant settled water (6)

- Potassium Permanganate

Table IV presents the results of some preliminary studies investigating the effects of potassium permanganate on natural precursors from the Ohio River. In these experiments, the percent removals of precursor are relatively small, the highest is 19 percent, the lowest is 3 percent. Thus, potassium permanganate does not have large influence on the precursors that are in the Ohio River, although it does do some good. As mentioned in a previous paper (5), permanganate may have a more dramatic effect on precursors in some waters where precursors were observed to react more like m-dihydroxy phenyl moieties.

Table IV PRELIMINARY DATA ON PRECURSOR REMOVAL FROM OHIO RIVER WATER BY POTASSIUM PERMANGANATE

$KMnO_4$ Reaction			Chlorine Reaction Time (hours)	ΣTHM µg/L	% Removal
Amount Added (mg/L)	Reaction Time (hours)	pH			
0	1.5	7.1	2	30.5	
5	1.5	7.1	2	25.7	15.4
0	1.5	9.3	2	52.3	
5	1.5	9.3	2	50.9	2.7
0	1.5	10.2	2	57.2	
5	1.5	10.2	2	54.0	5.6
0	0.5	Neutral 7.0	30	120.5	
5	0.5	Neutral 7.0	30	97.6	19.0

Adsorption

- Powdered Activated Carbon

Figure 9 presents some typical data on the performance of powdered activated carbon (PAC) for precursor removal. In this experiment chloroform formation potential declined some initially, and then decreased more slowly as a 100 mg/L dose was approached. These data would tend to indicate that a 5 or 10 mg/L PAC dose would give an effect that might be favorable if a finished water had a trihalomethane concentration just above the proposed regulation, but PAC could not completely eliminate precursor even with an uneconomically high dose.

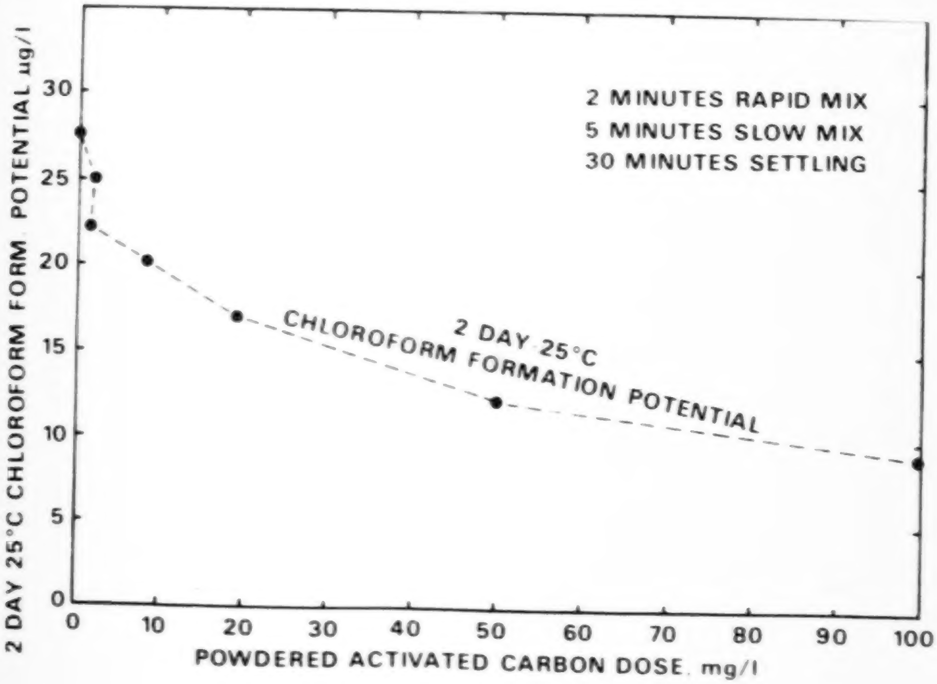


Fig. 9 Influence of powdered activated carbon on chloroform formation potential

- Granular Activated Carbon

Figure 10 shows data from a treatment plant in Huntington, West Virginia, U.S.A. The precursor is nearly completely removed initially and then the concentration steadily rises in the adsorber effluent, reaching the proposed maximum contaminant level (MCL) after about four weeks. Notice that the empty bed contact time here is only 6-1/2 minutes, which is a short empty bed contact time. Nevertheless, when the granular activated carbon is fresh, it will remove precursor well, but then a slow steady break-through occurs. Other data with deeper beds (longer empty bed contact time) tend to show that the time period for break-through to the proposed MCL is longer, Figure 11. Figure 12, data from the granular activated carbon treatment of water with a very high concentration of trihalomethane precursor, again demonstrates the influence of empty bed contact time.

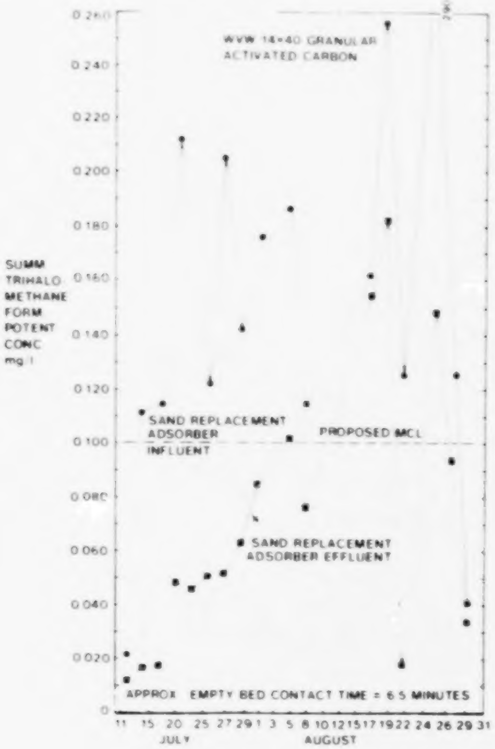


Fig. 10

Removal of trihalomethane precursors by granular activated carbon beds

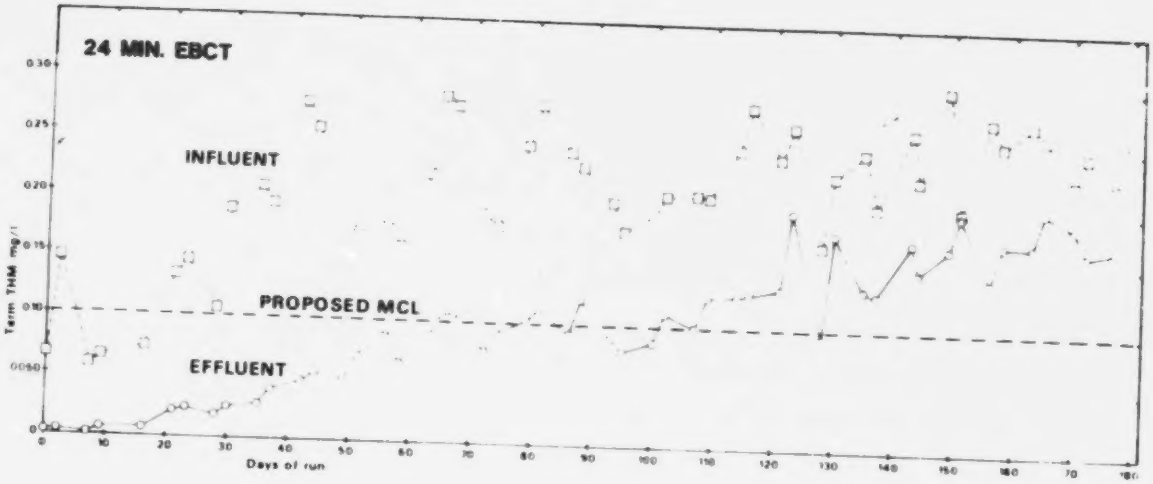


Fig. 11 Performance of terminal THM through Post Filter Adsorber run 1 (Feb.-Oct.1977) Jefferson Parish, La,

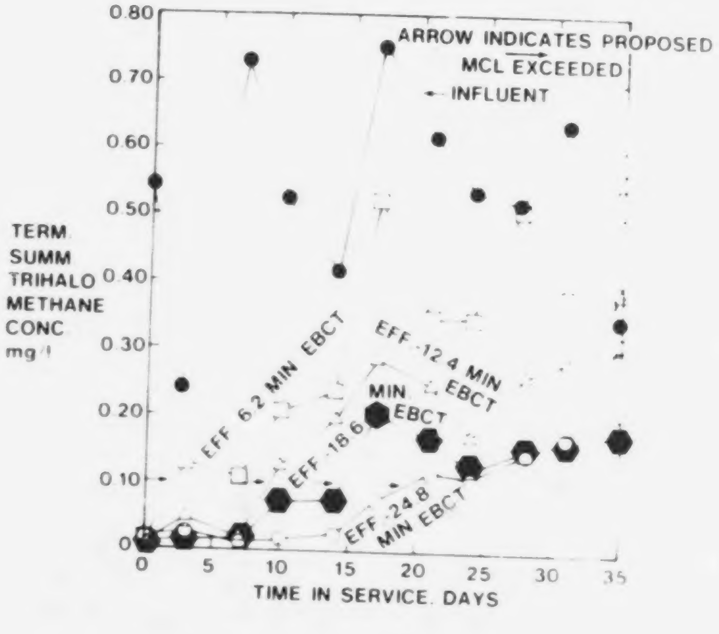


Fig. 12 Example of the influence of empty bed contact on terminal summation trihalomethane removal

- Ozone Enhanced Biologically Active Carbon Filters

A study on the utility of preceding granular activated carbon by ozone treatment on the removal of trihalomethane precursor was conducted in a pilot plant treating settled Ohio River water. The data in Figure 13 show that preceding the adsorption system by an ozone dose of about 1 mg/L, contact time 20 minutes, did result in a reduction in trihalomethane precursor in the adsorber effluent at any given service time when compared to conventional granular activated carbon. Both adsorption systems had a 9 to 10 minute empty bed contact time. The mechanism for this improved performance is thought to be related to an enhancement of biological activity in the activated carbon adsorber brought on by the ozone pretreatment.

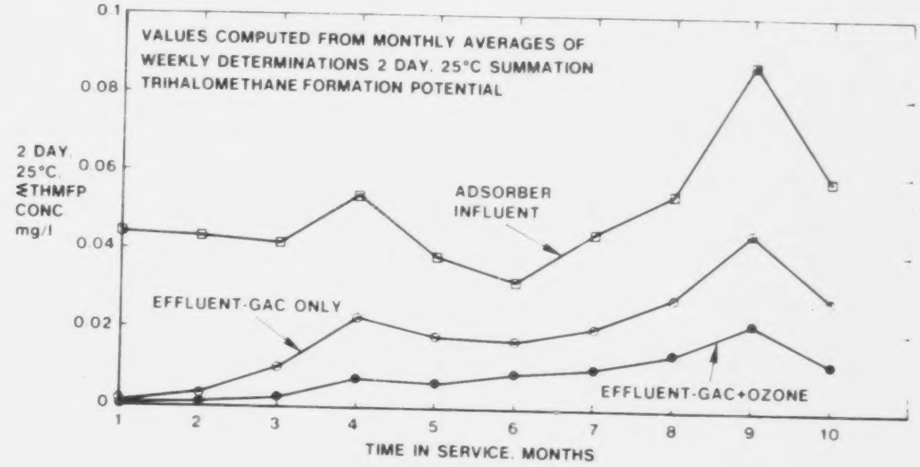


Fig. 13 Influence of ozonation prior to adsorption on trihalomethane formation potential removal

SUMMARY

Precipitation, oxidation, and adsorption are all methods of removing trihalomethane precursor. Of these various techniques, only adsorption on fresh granular activated carbon is completely effective, although the capacity of the activated carbon is finite. The other techniques, alum or iron coagulation, oxidation with ozone, chlorine dioxide or potassium permanganate, or adsorption with powdered activated carbon, are only partially effective but may still have a role in controlling trihalomethane concentrations in some cicumstances.

(1) SYMONS, J.M.
Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes
U.S. Environmental Protection Agency, Cincinnati, Ohio, 48 pp. plus 4 Appendices, Unpublished (June 1976)

(2) LOVE, O.T., Jr., CARSWELL, J.K., MILTNER, R.J., SYMONS, J.M.
Treatment for the Prevention or Removal of Trihalomethanes in Drinking Water
J. AWWA (in Press)

(3) SYMONS, J.M., CARSWELL, J.K., CLARK, R.M., DORSEY, P., GELDREICH, E.E., HEFFERNAN, W.P., HOFF, J.C., LOVE, O.T., Jr., McCABE, L.J., STEVENS, A.A.
Ozone, Chlorine Dioxide, and Chloramines as Alternatives to Chlorine for Disinfection of Drinking Water, State-of-the-Art
Summary in Proceedings of Second Conference on Water Chlorination: Environmental Impact and Health Effects, Gatlinburg, TN, Oct. 31 - Nov. 4 1977 (1978), 555-560, Complete version available from Director, Drinking Water Research Division, U.S. Environmental Protection Agency, Cincinnati, OH, 45268

(4) TRUSSELL, R.R.
Factors Influencing the Formation of Trihalomethanes
James M. Montgomery Consulting Engineers, Inc., Pasadena, CA, presented at the California-Nevada Section AWWA Seminar on Organics in Domestic Water Supplies, Palo Alto, CA, April 12, 1978

(5) STEVENS, A.A. et al.
Formation of Non-Polar Organochloro Compounds as By-Products of Chlorination
Presented at Conference on Oxidation Techniques in Drinking Water Treatment, Sept. 9-13, 1978, at Karlsruhe, Federal Republic of Germany

(6) MILTNER, J.J.
The Effect of Chlorine Dioxide on Trihalomethanes in Drinking Water
M.S. Thesis, University of Cincinnati (1976)

UNWANTED BY-PRODUCTS OF CHLORINATION

B. Josefsson

It is a challenge for an analytical chemist to determine the different organic compounds (in the nanogram per litre level) which are present in drinking water. For practical reasons I think it is meaningless to analyse all of them.

A hierarchic analytical system for the analysis of chlorinated compounds should begin with the determination of elemental chlorine for rapid screening of many samples. In this way it is possible to locate sources of organic chlorine compounds to the raw water or during water treatment processes. When this procedure reveals a source, a more laborious analytical determination of specific compounds can be performed. Dr. W. Kühn showed in his lecture that elemental chlorine analyses can be carried out with the DOCl (dissolved organic chlorine measured by pyrohydrolysis) method and DOClN (dissolved organic chlorine-nonpolar, measured with microcoulometry on a nonpolar solvent extract) (1). Other methods in this respect include non-destructive neutron activation analysis (NNAA) on elemental chlorine and bromine (2). When NNAA techniques are used it is possible to distinguish between chlorine and bromine, which cannot be done by coulometric methods, for example.

Liquid-liquid extraction with a nonpolar solvent is very practical for the determination of lipophilic organic halogens which can easily bioaccumulate. By using this method organohalogenated compounds can be tested for possible persistence by treating the extract with conc. sulphuric acid, UV light etc. Bioaccumulation and persistence are important in view of chronic or long-term effects, aspects which have not been discussed here.

In water treatment processes chlorine is widely used; however, chlorine dioxide has gained popularity especially when taste and odour problems occur upon conventional chlorination. Chlorine and chlorine dioxide have also been extensively used in pulp bleaching processes and much of the experience gained from these processes may be of great value for water chemists. Bleaching of pulp to eliminate miscoloring substances, e.g. lignin, are to some extent similar to oxidation of humic substances in water with different chlorine species. However, there is a pronounced difference in the concentrations of organic materials in the two processes.

Recent studies on by-products formed upon pulp bleaching with chlorine species have revealed great numbers of chlorinated organic compounds of both polar and nonpolar character in effluent water. The total amount of chlorinated compounds exceeds 1 ppm, expressed as chlorine in both polar and nonpolar solvent extracts of the effluent water (3). Only about a tenth of the total amount of lipophilic chlorine has been characterized, e.g. chloro-cymenes, chlorinated terpenes etc. (3) (4). The specific non-volatile compounds which cannot be separated gaschromatographically are still not very well studied. This deficiency may be partly overcome by use of chlorine detectors in liquid chromatography. The waste effluents from bleaching exhibit mutagenicity with the Ames test (5). Through the polar character of chlorophenols (from lignin breakdown), these substances have been found accumulated in fishes caught near the bleaching waste outlet (6).

Chloroform concentrations are about a hundred times higher in chlorine bleaching effluents than in drinking water (7). Hypothetically, some of the other chlorinated compounds found in pulp bleacning effluents may also be present in drinking water at a two- or three-order of magnitude lower concentration. If they are present in drinking water, do they have a long-term effect?

(1) KÜHN, W., SONTHEIMER, H., STIEGLITZ, L., MAIER, D., KURZ, R.
Use of Ozone and Chlorine in Water Utilities in the Federal Republic of Germany
J. AWWA 70 (1978), 326-331

(2) LUNDE, G., GETHER, J., JOSEFSSON, B.
The Sum of Chlorinated and of Brominated Non-Polar Hydrocarbons in Water
Bull. Environ. Contam. Toxicol. 13 (1975), 656-661

(3) EKLUND, G., JOSEFSSON, B., BJÖRSETH, A.
Determination of Chlorinated and Brominated Lipophilic Compounds in Spent Bleach Liquors from a Sulphite Pulp Mill. Glass Capillary Column Gas-Chromatography - Mass Spectrometry - Computer Analysis and Identification
J. Chromatogr. 150 (1978), 161-168

(4) LINDSTRÖM, K., NORDIN, J.
Identification of Some Neutral Chlorinated Organic Compounds in Spent Bleach Liquors
Sv. Papperstidn. 81 (1978), 55

(5) ANDER, P., ERIKSSON, K-E., KOLAR, M-C., KRINGSTAD, K., RANNUG, U., RAMEL, C.
Studies on the Mutagenic Properties of Bleaching Effluents
Sv. Papperstidn. 80 (1977), 454

(6) LANDNER, L., LINDSTRÖM, K., KARLSSON, M., NORDIN, J., SÖRENSEN, L.
Bioaccumulation in Fish of Chlorinated Phenols from Kraft Pulp Mill Bleachery Effluent
Bull. Environ. Contam. Toxicol. 18 (1977), 663-673

(7) EKLUND, G., JOSEFSSON, B., ROOS, C.
Determination of Volatile Halogenated Hydrocarbons in Tap Water, Seawater and Industrial Effluents by Glass Capillary Gas Chromatography and Electron Capture Detection
J. High Resol.Chrom. 1 (1978), 34-40

OCCURRENCE OF VOLATILE ORGANOHALOGEN COMPOUNDS IN THE OPERATION OF WATERWORKS WITH VARIOUS TYPES OF WATER AND AMOUNTS OF CHLORINE

S. Normann

Since the occurrence of low-boiling organic halogen compounds in drinking water became known their formation in the waterworks as a function of the operating conditions has been of particular interest. Detailed investigations on this problem were also started at the municipal works in Wiesbaden. The following contains a brief report on the most important results.

Use of chlorine in the Wiesbaden water supply

In Wiesbaden chlorine is added at several points:

1) In WI-Schierstein Rhine water is treated by flocculation, filtration, and activated carbon filtration and then by seepage for the purpose of artificial ground water enrichment. The first measure is to chlorinate the raw water from the Rhine for the purpose of oxidizing ammonia and for disinfection. The amount of chlorine added is such that after a few minutes 0.5 mg/l of free chlorine is still detectable.

2) The drinking water obtained from the artificially enriched ground water - containing a considerable proportion of bank filtrate from the Main - after a further treatment by aeration and slow sand filtration, is chlorinated to maintain hygienic safety to the extent that it leaves the works with 0.4 to 0.5 mg/l of free chlorine. PAC filtration will be added to the treatment.

3) A ground water charged with a small amount of anthropogenic material from the Hessisches Ried, transported over 50 km to the supply area of Wiesbaden, must be chlorinated several times on the way so that bacteriological safety is

ensured for the various smaller consumer communities situated along the transport route, and on the other hand so that the limiting chlorine level is not exceeded at any point.

Halomethane formation in the chlorination of raw water and drinking water

It is worthwhile to compare the action of raw water chlorination and drinking water chlorination in Schierstein as regards the formation of organic chlorine compounds, and also to compare the two drinking waters that come from very different sources.

The three waters were studied gas-chromatographically for at least 6 months for the content of organohalogen compounds (after enrichment by pentane extraction and using an electron-capture detector) and the low-boiling fractions were determined quantitatively. In addition to this, the DOC and the UV absorption at 254 nm were measured as sum parameters for the organic loading. The mean values from about 20 samples for halomethanes, the sum parameters, and the amounts of chlorine added are listed in Table 1.

As regards the concentrations of halomethanes, it is noteworthy that these may be affected by an error resulting from the unreliability of the determination of the partition coefficients. With an enrichment factor of 200, a recovery rate of 10% for chloroform and 33% for the other halomethanes was calculated.

The interpretation of the results shall thus be restricted to the relationship of the individual values to one another. Some interesting statements can then be made:

Table 1 Mean values for halomethane formation in Wiesbaden waters

Halomethane concentration in µg/l	Rhine water				Ground water from Hessisches Ried
	Raw water		Drinking water I		Drinking water II
	not chlorinated	chlorinated	not chlorinated	chlorinated	chlorinated
Chloroform	1.0	3.0	2.5	2.5	4.0
Carbon tetrachloride	0.3	1.2	0.15	0.15	0.1
Bromodichloromethane	0.06	4.5	1.2	5.0	4.5
Dibromochloromethane	not detected	1.2	0.15	10.0	0.3
Bromoform	rare	n.detect. ...1.0	not detected	5.0	not detected...0.1
Chlorine addition, g/m^3	5.5		0.75		1.4
DOC, g/m^3	4.5		1.8		2.0
UV absorption at 254 nm, m^{-1}	9.8		3.3		3.6

1. The halomethane formation during the chlorination of raw water from the Rhine is only of the same order of magnitude as that during the chlorination of drinking water. This is surprising, because the organic loading and also the chlorine consumption in the raw water is much greater than those in drinking water. It must therefore be assumed that Rhine water contains relatively few halomethane precursors.

2. Each compound shows different behaviour in different waters.

3. The relatively sharp increase in the bromine compounds is striking in all three waters.

4. Comparison of the two drinking waters clearly shows that even in the safety chlorination of a natural, organically weakly loaded ground water halomethanes are formed in low concentrations. In respect of the chlorine compounds listed the two drinking waters show approximately the same loading. The formation of dibromochloromethane and bromoform in drinking water I can be explained by the higher bromide contents in the enriched Schierstein ground water.

Formation of organohalogen compounds in chlorination of raw water with variation of the amounts of chlorine added.

The effect of various chlorine additions and of various excesses of chlorine in the chlorination of raw water was investigated in a series of operational trials at the Rhine water treatment works lasting several weeks. The chlorine was added directly before the addition of the flocculation agent. The effect of the chlorination was studied after flocculation and filtration and a mean action time of 8 h.

Table 2 Quality parameters in the four chlorination trials (mean values)

Experimental period	Mean chlorine addition g/m^3	Chlorine concentration in flocculation inflow g/m^3	Water temp. ^{o}C	pH	NH_4^+ mg/1	DOC mg/1	CSB $KMnO_4$ mg/1	UV_{254} m^{-1}
12.12.77 to 11.01.78	8.0	1.1	4.4	6.97	0.62	4.9	21.7	10.7
17.01.78 to 18.02.78	6.5	0.5	3.8	7.11	0.76	5.0	21.1	10.4
21.02.78 to 11.03.78	4.0	0.1	5.5	7.20	0.45	4.8	20.3	10.1
21.03.78 to 25.04.78	0	0	9.6	7.44	0.11	4.2	17.3	9.1

In Table 2 are listed the quality parameters of the raw waters as mean values for the experimental period for the four different additions of chlorine in the range between 0 and 8 g/m^3. The lower concentration of free chlorine in the flocculation inflow shows that the bulk of the chlorine is consumed after only a few minutes. Not until a dose of 8 g/m^3 can appreciable residual concentrations of free chlorine be measured, which act further during the subsequent treatment.

The gas-chromatographic measurements were performed at three temperatures, namely at 60°, 180°, and 230°C. Fig. 1 shows

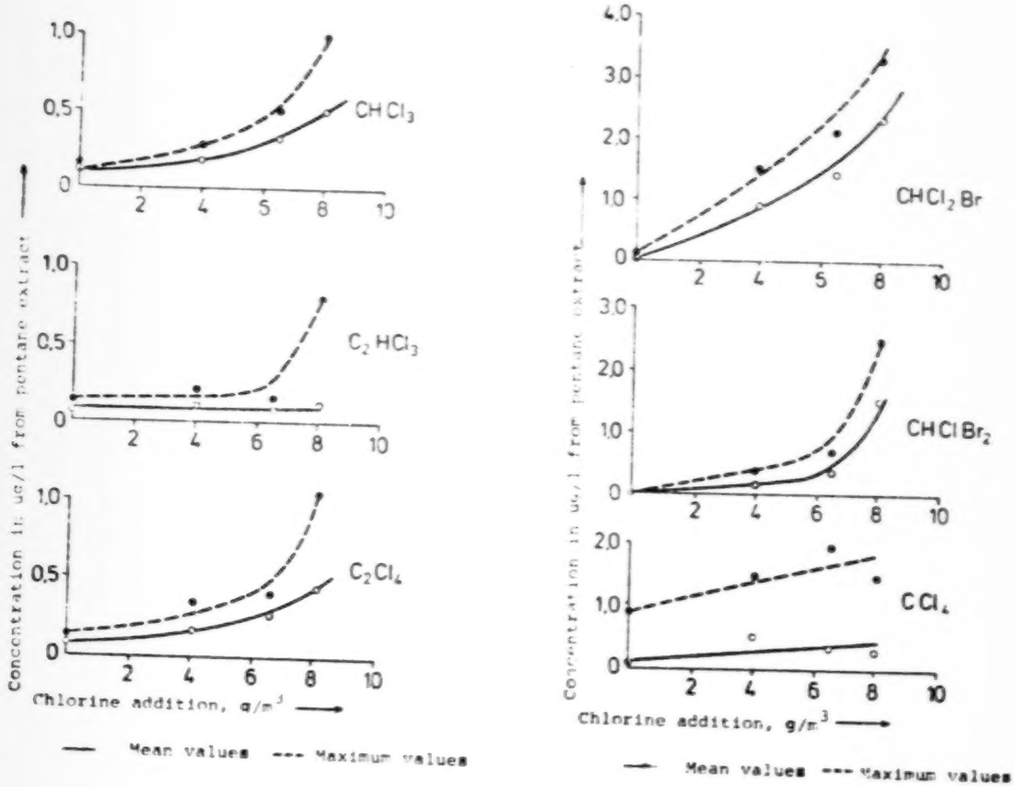


Fig. 1 Formation of low-boiling organohalogen compounds in the chlorination of raw water in dependence on the amount of chlorine added.

the concentration increase for 6 different readily volatile organohalogen compounds with increasing doses of chlorine. In addition to the mean values, the maximum concentrations found are also indicated, since they exhibit trends still more clearly.

The concentration data refer here to values measured in pentane, recalculated to the amount of water used but not yet taking into consideration the partition coefficients for the pentane-water system.

The different courses of the curves show clearly that the formation of the individual compounds is strongly dependent on the amount of chlorine: while some compounds are only formed with larger chlorine amounts, or when the chlorine is in excess (e.g. trichloroethylene), in the majority of compounds elevated concentrations can be detected after only small chlorine additions. The strongest dependence is given for bromodichloromethane. For the remaining compounds appreciable concentration increases are only measured when the chlorine addition exceeds 6 g/m^3, i.e. in the range where an excess of free chlorine is already present.

Most of the substances formed during chlorination are already present in low concentrations in Rhine water. Only very few new compounds are formed, and these only at high doses. These are low-boiling substances. In addition to dichlorobromomethane, seven new compounds were detected at a column temperature of 60°C; at 180°C only two were found in low concentrations.

As regards the higher-boiling substances (column temperature 180°C), the concentrations of the first four were increased by the addition of chlorine - these were probably dichlorobenzene, hexachloroethane, trichlorobenzene, and hexachlorobutadiene.

The concentration of the higher-boiling compounds is sometimes decreased by the flocculation (by up to 50%). Even with high chlorine additions an increase was never observed.

An important factor for the evaluation of the effects of the concentration increase of organic halogen compounds is the ease of their removal during the subsequent activated carbon filtration.

This was also studied, and in addition longer operational experience is already available in this case. The types of carbon used (F 300 and F 400) are very effective as regards the elimination of the DOC and the removal of high-boiling nonpolar chlorine compounds. The highly-volatile halogen compounds formed mainly by the chlorination, however, are only partially adsorbed even by fresh carbon (e.g. chloroform and carbon tetrachloride), or pass through the filter already after a loading of only 10 l/g carbon (e.g. bromodichloromethane and dibromochloromethane). With increasing loading of the carbon these compounds can be found in the filtrate long after they can no longer be detected in the raw water. The high-boiling compounds (starting with bromoform) occur only sporadically in the filtrate, in low concentrations.

Summary

The operational trials on the chlorination of raw water with various amounts of chlorine, performed on moderately polluted Rhine water (with average outflow), show clearly as regards the gas-chromatographic substances that low-boiling organohalogen compounds are formed first. The dependence on the chlorine dose is very different for different compounds. With low-dosage chlorination of the raw water with doses below 6 g/m^3 - as in the Rhine water treatment works at Schierstein - the concentrations of readily volatile organohalogen compounds formed are kept within permissible limits.

They are approximately in the same range as in the chlorination of drinking water.

If up to now chloroform formed the centre of interest, in the case of the chlorination of bromide-containing waters the bromine-containing halogen compounds must receive more attention than previously, because these compounds too are insufficiently eliminated by the activated carbon filtration and form in appreciable concentrations even under the conditions of low-dosage chlorination of drinking water. In this connection the bromide content of the water also gains in importance.

On the example of a marsh water (Hessisches Ried) it was demonstrated that the safety chlorination necessary when water is transported over a long distance requires relatively high doses of chlorine, and so can give rise to appreciable halomethane concentrations.

THM FORMATION IN TWO DIFFERENT WATER TREATMENT SYSTEMS AT ROTTERDAM

J.J. Rook

1) Rotterdam Waterworks owns two treatment plants, i.e. the Berenplaat Plant, dating from 1966, with a production capacity of 12.000 m^3/h, and the new Kralingen Plant, capacity 5.000 m^3/h, which started production in July 1977.

Both plants treat the same type of raw water, which is stored river Maas water. In the Berenplaat Plant conventional chemical treatment is applied; breakpoint chlorination, dosage of PAC, coagulation with Fe (III), sedimentation, rapid filtration, post chlorination.

The new Kralingen Plant consists of primary coagulation, floc removal by means of lamella separators, ozonation, dual media filtration and filtration through granular activated carbon, post chlorination.

The raw water has been stabilized by self-purification. Algae control measures have proved to be very effective, the average chlorophyll content being 5 ppb, with incidental peaks of 40 ppb. The TOC value averages 5,5 ppm, mainly caused by natural yellow acids which are identical with fulvic acids. The raw water is transported through 28 - 30 km pipelines. During the summer period of 1977 the raw water was pre-chlorinated (dosage circa 5 ppm) before transport in order to keep pipe walls clean from bacterial growth. During the winter season no chlorination was applied. Transportation to Berenplaat takes 6 h, to Kralingen 15 h. With the given amount of fulvic acids the pre-chlorination resulted in THM formation:

Plant	Contact time	Temp.	TTHM at plant intake
Berenplaat	6 h	12-22°C	68 ppb
Kralingen	15 h	12-22°C	103 ppb

During the winter season of 1977-78 pre-chlorination was interrupted. Consequently, no THM formation occurred.

Results of conventional treatment

Table I summarizes the THM contents in the finished water of the conventional treatment at Berenplaat, both with and without pre-chlorination.

TABLE I THM in Berenplaat Plant
Conventional: Breakpoint-PAC-coag.-filtr.

		$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total
12-22°C	Raw water pre-chlorinated (5 ppm 7 h)	30	22	14	1.5	68
	Finished water	40	28	14.5	1.5	84
1-12°C	Raw water not chlorinated	<1	0	0	0	<1
	Finished water (4 ppm breakpt.chlor.)	18	13	6	1	38

This data shows that post-chlorination (0.8 ppm) caused an increase of TTHM from 68 ppb to 84 ppb during the summer season.

The formation potential of the raw water was 160 ppb after 48 h at 20 °C.

TABLE II THM in Kralingen Plant
Coag. 2.5 ppm ozone-filtr. (GAC)

		$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total
12-22°C	Raw water pre-chlorinated (5 ppm 15 h)	50	32.5	18	2.5	103
	after Floc Separation	32	22	13	1.5	68
	after Ozonation	32	23	12	2	69
	Finished water (without GAC) (0.8 ppm 6 h post-chlorin.)	49	35	16.5	1.5	102
1-12°C	Raw water not chlorinated	1	0	0	0	1
	after Coag.+ Ozone	1	0	0	0	1
	eluted from GAC (7-10 months in use)	5	3	1.5	0	9.5
	Finished water (post-chlorinated)	6.5	6.5	9.5	6.5	29

TABLE III THM in Kralingen Plant
Influence GAC

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total
after GAC (first month)	1.2	0.8	0	0	2
after GAC post-chlorin. (0.8 ppm 6 h)	3.2	3.7	5.4	5.7	18
after GAC (2-5 months in use)	17	11	4	0	32
after GAC post-chlorin.	18	12.5	13.5	8.5	52

In the winter period when only breakpoint chlorination with a chlorine dosage of 4 ppm at a contact time of 30 min. was applied, the finished water contained 38 ppb TTHM.
It is interesting to compare this figure with the results of the ozone-GAC treatment in the Kralingen plant.

Results of new treatment plant

In the Kralingen plant the reservoir water is coagulated with iron, followed by ozonation (3 ppm), dual media filtration and final filtration through activated carbon (GAC, contact time 12.5 min.).

The plant was started in July 1977, when the raw water was pre-chlorinated. During 15 h transportation TTHM went up to 103 ppb. In the first month of operation the carbon filters could not be used, because they were in the process of being filled.

The effects of this treatment coagulation and ozonation without carbon are shown in Table II. It is seen that the THM once formed by pre-chlorination is only partly removed by the coagulation and ozonation steps. An interesting observation is that post chlorination of 0,8 ppm gave rise to renewed THM production, i.e. an increase from 69 to 102 ppb. The TOC value after coagulation ozonation was 2.8 - 3 ppm.

The advantageous effect of the adsorption of both precursor and THM onto fresh carbon may be seen from the data in Table III, upper lines. The TTHM in the raw water still amounted to 100 - 103 ppb. Adsorption reduced this to 2 ppb. The observation that post-chlorination (measured after 6 h) produced 18 ppb TTHM, as compared to 33 ppb without GAC, indicates that precursors remaining after ozonation were partly reduced. During this first month of operation the carbon filter treatment lowered TOC from 3 ppm to 0.9 ppm. In the next three months, however, the TOC of the effluent gradually rose to 1.5 ppm.

During this period THM breakthrough started to become significant for $CHCl_3$ (Table III, lower case). The more brominated THM were withheld longer.

Precursor removal was still performed at a slightly diminished level. Post-chlorination now caused a 20 ppb increase of TTHM (32 to 52 ppb).

During the following winter season the pre-chlorination was interrupted and consequently THM formation did not occur. The results of the ozone - GAC - post-chlorination treatment are given in the lower case of Table II.

Two conclusions may be drawn. First, the THM orginally adsorbed was slowly eluted, resulting in average values over the 4 winter months of 9.5 ppb TTHM. Secondly, precursor removal appears to remain at about the same level as indicated by the 20 ppb increase caused by post chlorination.
However, the effect of lower temperature on the overall reaction rates have to be taken into account.

Table IV summarizes the observations reported here.
The data clearly show that pre-chlorination of raw water is deleterious to any further conventional or advanced treatment. Starting with non-chlorinated raw water in the conventional treatment resulted in 38 ppb TTHM, as compared to 20 ppb TTHM increase during 6 h post chlorination. In this case the total effect was negatively influenced by the elution of 9 ppb TTHM resulting from the preceding period during which the raw water had been chlorinated.

A final observation is that ozone treatment resulted in a shift towards brominated THM in post chlorination, as shown by the data of the finished waters of the conventional treatment (Table I, last line) vs. new treatment Tables II and III.

TABLE IV

TTHM PLANT I Conventional		TTHM PLANT II Ozone GAC	
	ppb		ppb
Raw water not chlorinated	1	Raw water not chlorinated	1
		Coag.-Ozone-GAC (6-10 months)	9
Finished water	38	Finished water	29
Raw water prechlorinated	68	Raw water prechlorinated	103
		Coagulation-Ozone	69
Finished water	84	Coag.-Ozone-GAC	32
		Finished water (0.8ppm post chlorinated)	52

CHEMICAL CHANGES AND REACTION PRODUCTS IN THE OZONIZATION OF ORGANIC WATER CONSTITUENTS

E. Gilbert

The growing interest in the use of ozone for the treatment of drinking water and waste water has led not only to studies on the process techniques for the ozone input (1-10), the mass transfer from gas- to water phase (11-13), and the behaviour of ozone in water (14-20), but also to a large number of publications on the chemical effect involved. The following is a survey of the reactions of ozone with the organic constituents of water and of the oxidation products produced in this way.

Disinfectant effect

Until the nineteen-fifties ozone was used mainly for its disinfectant effect; it had been used in the treatment of drinking water as early as the turn of the century (21), and therefore the majority of publications have concentrated on this partial aspect. In addition to more recent results on its disinfectant action and on viral inactivation by ozone (22-27), attention is particularly drawn to the proceedings of the 1976 Chicago conference "Forum on Ozone Disinfection" (28).

Since the analysis methods are extremely complicated, very little can be said about the mechanism of disinfection or the inactivation of viruses, which can often take place in a matter of seconds with a dose of 1 mg O_3/l. The first insight into the chemistry of the disinfection processes was provided by trials on amino acids, the building blocks of proteins, in pure solutions. Mudd et al.(29), Menzel (30), and

Shuval (31) reported that the unsaturated amino acids such as tryptophan, tyrosine, histidine, and the sulphur-containing amino acids such as methionine, gluthathione, cystine, and cysteine are readily attacked by ozone. Shuval (31) found that viruses react with ozone at much the same rate as the above-mentioned amino acids (Fig. 1, ozonization of tryptophan). This is an indication that the inactivation of viruses may be due to an attack of ozone on these amino acids and that as a result of oxidation the acids lose their structural characteristics important for biological activity. In the case of the unsaturated amino acids, such as tryptophan, the double bond is attacked and the molecular structure is destroyed (Fig. 2). In the sulphur-containing amino acids the sulphur is oxidized to sulphoxide, sulphone or to sulphonic acid, whereby the acids can no longer act as oxygen carriers in redox processes. It is not known whether the oxidation products themselves have any disinfectant action, since their identification has been only partial and qualitative.

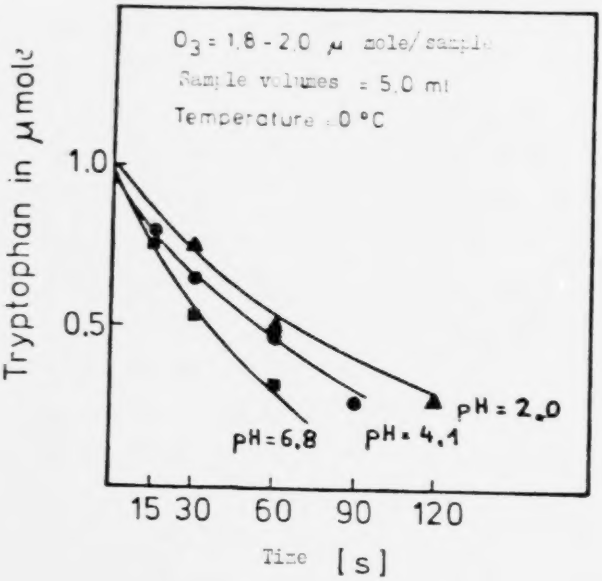


Fig. 1

Reaction of tryptophan with ozone; dependence on the pH

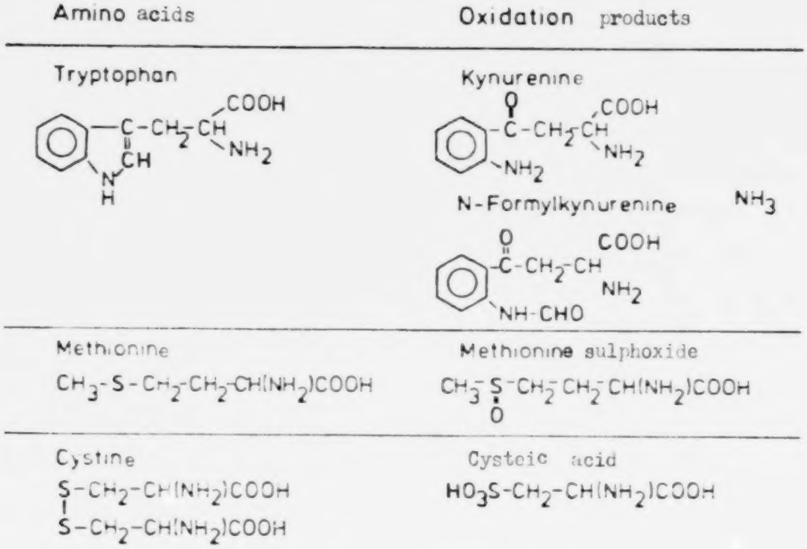


Fig. 2 Ozonization of amino acids; oxidation products

Effect on the sum parameters

Besides the disinfectant effect of ozone which, as already explained, may be associated with the ready oxidizability of amino acids, its other beneficial effects have been utilized for a considerable time. These are an improvement of the water's odour and taste (32-36), removal of any colour or a reduction of UV-extinction (32, 37-45), as well as a reduction in the molecular weight of high-molecular substances (46-50). Fig. 3 shows as an example the effect of ozonizing humic acid from Hohlohsee (Northern Black Forest) on the size of its molecule. After a dose of only 1.5 mg O_3/mg C, half of the carbon is present in the form of molecules with molecular weights below 1000 (50).

The DOC and the COD are also decreased by oxidation processes. It is found that the DOC decreases much more slowly than the COD and that with longer ozonization times both approach asymptotically to a final value. To illustrate this point the results obtained in the ozonization of 2-nitro-p-cresol in water are shown in Fig. 4. An unbuffered 1 mmol solution at pH 5 was used. The greatest decrease in the two parameters occurs after degradation of the cresol, i.e. the products formed are present in a higher oxidation state and - at least in the acid range - react further with ozone only very slowly.

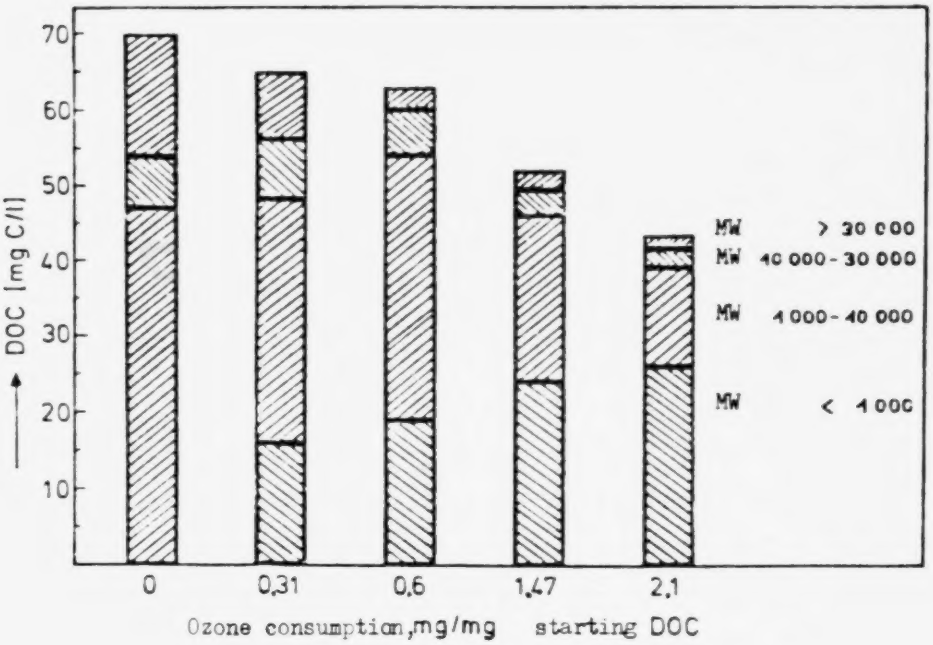


Fig. 3 Ozonization of humic acid (Northern Black Forest) without the molecular weight fraction > 1000

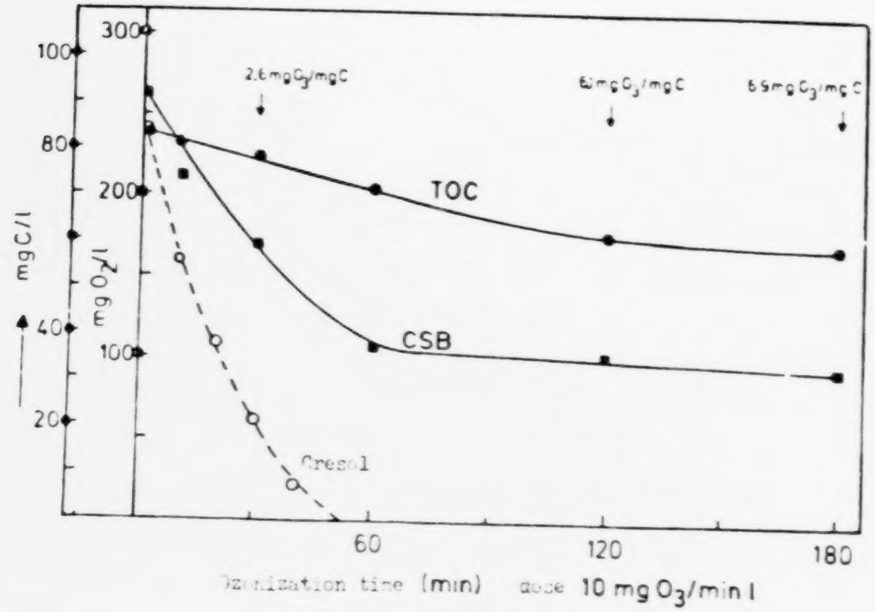


Fig. 4 Ozonization of 2-nitro-p-cresol (c = 1 mmole/l) TOC and COD decrease in dependence on the ozonization time

In a further example, which is representative of many (38, 39, 43-45, 48, 51-69, 120, 134) a paper pulp waste water was studied (51). As Fig. 5 shows, with a limited ozonization time a total degradation to CO_2 and H_2O is not achieved. The extent of the COD reduction naturally varies from one substance class to another, and in the case of a given waste water reacts according to its composition. After the COD has been decreased by 50-70% further ozonization brings about only a negligible reduction of this parameter.

According to the present data, a reduction of the COD value by 1 kg is attained by the consumption of 1-4 kg of ozone (Table 1), and in extreme cases even 6-10 kg of ozone may be necessary.

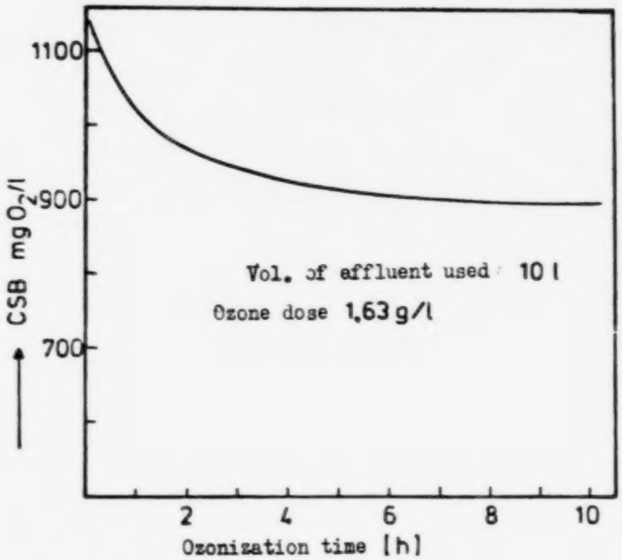


Fig. 5

Ozonization of paper mill effluent; COD decrease in dependence on ozonization time

TABLE 1 COD degradation and ozone consumption

Solution used	COD_o — COD_t mg O_2/l	Ozone consumption / Δ COD	Ref.
Ca ligninsulphonate	1130 → 890	1	51
Paper mill effluent	4950 → 2500	1,8	
Effluent	225 → 198	1,5	38
Industrial effluent	3340 → 1930	0,8	57
	3340 → 314	1,8	
	2140 → 1620	2,5	
	910 → 160	5,0	
Effluent from a sauerkraut factory	14000 → 3000	2,0	62
Industrial effluent	156 → 94	0,7	66
Paper mill effluent	1480 → 1150	1,4	44
Discharge from clarification plant	59 → 49	1,4	46
	59 → 35	2,0	
	58 → 50	1,5	
Discharge from clarification plant	48 → 24	2,5	60
Discharge from clarification plant	43 → 42	5,6	58
	56 → 32	1,7	
Discharge from clarification plant	80 → 16	2,5	63
	20 → 10	2,5	
Humic acid solution	240 → 60	2,7	52
Naphthol	26 → 19	11	61
Phenol	70 → 24	1,6	
Chlorophenols	216 → 106	1,5 - 2,3	72
Naphthalene-2,7-disulphonic acid	265 → 60	2,5	54
p-Toluenesulphonic acid	250 → 60	3,7	--

With small ozone doses an increase of the COD has actually been observed in some cases (43, 61, 64, 68, 69). In the first phase of the ozonization some substances are made accessible to the COD analysis by the oxidation, thus producing an increase in COD which then decreases again as the ozonization continues.

The biological degradability is often improved by the attack of ozone, as has been reported in many recent papers. Data on the rise of the BOD_5/CCD ratio after ozone treatment are found particularly in (38, 44, 45, 54, 65, 70-72).

The change in the molecules after ozonization also influences the chlorination processes in the treatment of drinking water. Preliminary ozonization reduces the formation of chloroform during the subsequent chlorination (73-77). Maier (75) observed that as the chloroform decreased an equivalent increase of bromodichloromethane and dibromochloromethane took place in ozonized Lake Constance water. Lawrence (77) was able to establish that in the ozonization of ligninsulphonic acid and aspartic acid the concentration of "chloroform precursors" increased at the start of the reaction and only fell again as the oxidation progressed. Rook (73) found in addition that the ozonization effect contributing to the reduction of chloroform formation becomes the smaller, the longer is the interval between ozonization and chlorination.

In the large-scale plant at Lengg (Switzerland)(78) increase in the concentrations of two halogen compounds, dichlorobutanone and iododichloromethane, could be observed after ozonization. Block and Buydens found an increase of the chlorine demand after ozonization of raw water (79, 80). Maier (75) showed that after ozonization of Lake Constance water the chlorine consumption proceeded essentially more slowly than in non-ozonized water. In addition, several authors have described an increased repopulation with bacteria due to ozonization (75, 78).

Finally, the ozonization of raw water or river bank filtrate can lead to the formation of non-polar chlorine compounds (81).

The effects mentioned depend of course on the type of the raw water or on the composition of its constituents. The latter, however, are so numerous that so far the complex systems of raw water and waste water can in effect only be characterized with the aid of sum parameters. Therefore, the data concentrate on the action of ozone on such measurable parameters.

Ozonization of pure compounds

To explain and thereby also to control these phenomena, a knowledge of the exact compositon of the aqueous solutions would naturally be necessary. This is the first basic prerequisite for informative results. It also seems useful, as in the case of viral inactivation, to resort first to model substances and to study the ozone-oxidation on simple systems. This approach has been described in recent years by several working groups.

Quinoline

Naimie (82) ozonized 200 ml of a 0.25 - 0.5 mM quinoline solution (pH 6.9), which after 60 min (30 mg O_3/min) contained less than 10% of the initial quinoline content.

Cyclohexanol, cyclohexene

Cyclohexanol and cyclohex-1-ene-3-ol (2 g/l) in the presence of 10.5 g of $Ca(OH)_2$ were eliminated with 4 g/l or 1.5 g/l of ozone. Malonic acid, glutaric acid, adipic acid, and succinic acid were identified qualitatively among the oxidation products, but amounted only to an estimated 5% of the total amount of the oxidate (83).

Urea

Eichelsdörfer (84) was able to determine quantitatively the oxidation products of the ozonization of urea, CO_2 and nitric acid.

Malonic acid

The ozonization of malonic acid (85, 54) produced tartronic acid, mesoxalic acid, oxalic acid, CO_2, and H_2O_2. A mass balance was set up. In this process 192 ppm of ozone are consumed in 100% elimination of 104 ppm of malonic acid.

Maleic acid

Black (86) ozonized 40 g of maleic acid in 100 ml of water with the stoichiometric quantity of ozone for the preparation of glyoxylic acid.

Caffeine

Shapiro (87) found in the ozonization of caffeine (660 ppm) that 4.2 moles of ozone were necessary to eliminate 1 mole of caffeine. Dimethylparabanic acid was identified in addition to several other oxidation products.

Dichlorobenzene

The ozonization of dichlorobenzene in pure aqueous solutions (88) proceeded most efficiently at pH 8.4. 60 mg of ozone are needed to oxidize 30 mg of the substance/l.

Glucose

Walter (89) described the reduction in the COD after ozonization of 6 litres of 0.1% glucose solution. After a maximal dose of 1.6 g of ozone the COD fell by 10-15%.

Ethylenediaminetetraacetic acid

Krause (90) studied the decomposition of ethylenediaminetetraacetic acid chelates with ozone. To release 90% of the metals (Ca, Zn, Ni) from the chelate complexes in 1 litre of 0.01M solution an ozone amount of 1.7 - 3.4 g O_3/l was used. The reaction proceeds from pH 7 in the basic region twice as rapidly as in the acidic region.

Aliphatic alcohols

The ozonization of methanol (91, 91a, 92), ethanol, butanol, and octanol (92) proceeds via the aldehydes to carboxylic acids. 88% of isopropane is transformed into acetone (93). In the ozonization of ethanol, Gilbert (94) found in addition H_2O_2, short-lived peroxides, and formic acid (Table 2).

Alkylbenzenesulphonic acids

Buescher and Ryckman (95) investigated the behaviour of tert.alkylbenzenesulphonates (ABS) with respect to ozone. 12 mg of ozone were consumed to oxidize 4.5 mg of ABS. Evans (96) found that the removal of 15.6 mg of ABS in 1 litre of discharge from a biological clarification plant requires an ozone dose of 75 mg/l, and that the oxidation products are utilized better biologically. Kandzas (97) reports that at pH 11 90 mg of ABS are eliminated by 190 mg of O_3. Small quantities of formaldehyde and formic acid were found as oxidation products. Joy (98) studied the ozonization of nonyl- and decylbenzenesulphonates. 720 mg of O_3 were needed at pH 6 to degrade 160 mg of sulphonate and only 240 mg at pH 12. 70% of the sulphonic acid was converted into sulphate. Formic and oxalic acids were determined quantitatively and nonylglyoxal qualitatively as organic oxidation products (Table 3).

TABLE 2 Ozonization of alcohols

Compounds	Concentration	Ozone consumption	Degradation	pH	Ref.
Methanol	140 mg/150 ml	90 mg	29 %	5.5 - 5.5	92
Ethanol	210 mg/150 ml	360 mg	71 %	5.4 - 3.8	
Butanol	330 mg/150 ml	380 mg	64 %	6.2 - 3.7	
Ethanol	92 mg/l	211 mg	90 %	6.3 - 3.8	94
Isopropanol	192 mg/l	amount added 2.6 g	100 %	7	93

TABLE 3 Ozonization of alkylbenzenesulphonates

Compounds	Concentration	Ozone consumption	Degradation	pH	Ref.
Alkylbenzenesulphonate	4.5 mg	12 mg	100 %		82
"	15.6 mg	75 mg	100 %		83
"	90 mg	190 mg	100 %	11	84
Nonyl- and decyl-benzenesulphonate	160 mg	720 mg	100 %	6	85
	160 mg	240 mg	100 %	12	

Polycyclic aromatics

Reichert (99) and Gomella (100) studied the degradation of 3,4-benzpyrene. 0.7 ppm of ozone are required to remove 1 ppb of benzpyrene from water.

Chlorine-containing pesticides

The ozonization of pesticides has been studied by several authors (Table 4). Up to now the toxic dieldrin has been identified qualitatively as the oxidation product from aldrin and heptachloroepoxide from heptachlor (101). Brower (105) established in the fish test that the oxidation products of aldrin are less toxic.

TABLE 4 Ozonization of chlorine-containing pesticides

Pesticide	Concentration	Ozone dose	Ozone con- sumption	Degra- dation	pH	Ref.
Lindane	2 ppm	17 ppm		0		101
Endosulfan I	"	"		0		
Endosulfan II	"	"		12 %		
Dieldrin	"	"		26 %		
Heptachloroepoxide	"	"		26 %		
DDT	"	"		78 %		
Aldrin	"	"		86 %		
Heptachlor	"	"		100 %		
Lindane	40-100 ppb	0,4-3 ppm		0		102
Lindane	10 ppb	11 ppm		10 %		103
Lindane	50 ppb	149 ppm	97 ppm	100 %	9,8/6,8	104
Aldrin	20 ppb	23,8 ppm		100 %		105
Aldrin	0,005 % suspension	2,85 g		100 %	7,5-4,4	112
DDT	7 ppp			100 %	7,9-4,5	

Phosphorus-containing pesticides

In contrast to the chlorine-containing pesticides, the phosphorus-containing ones are more readily oxidized. Richard and Laplanche (106-108) found that after an ozone dose of 3 ppm 80 ppb of parathion were oxidized; toxic paraoxon is formed among other products, and is degraded only after 5 ppm of ozone has been added. 2,4-Dinitrophenol, picric acid, sulphuric acid were identified qualitatively and phosphoric acid quantitatively as the oxidation products (Table 5).

Waste water constituents

For a better control of the ozonization of waste waters from photographic processing laboratories, the individual constituents have also been studied (59,109), such as acetic acid, glycine, diethylene glycol, benzyl alcohol, and various colour developers. The concentrations amounted to 1 g/l and

TABLE 5 Ozonization of phosphorus-containing pesticides

Pesticide	Concentration	Ozone amount	Degradation	pH	Ref.
Malathion	100 ppb	5 ppm	88 %	8	106-108
Parathion	87 ppb	"	83 %		"
Methylparathion	125 ppb	"	84 %		"
Fenitrothion	120 ppb	"	93 %		"
Parathion	2500 ppb	149 ppm	100 %	9.8/6.5	104
Fenthion	2450 ppb	149 ppm	100 %	9.8/7.2	

the ozone dose to 0.5 g O_3/h. Ozonization was performed for 8 h and the COD decrease was measured. Glycine and acetic acid were the only substances tested that exhibited no change.

Bauch and Burchard (110) studied a series of organic substances and determined only the degree of degradation. The concentrations used were 1 - 2 g/l for methanol, ethanol, glycerol, ethyl acetate, acetic acid, caprylic acid, sugar, and glucose and 0.1 - 0.5 g/l for hydrazine, phenol, o-cresol, hydroquinone, o-salicylic acid, pyridine, benzine, chloroform, benzene, and toluene. Acetic acid, ethyl acetate, caprylic acid, pyridine, and chloroform were shown to be stable to ozone.

Caulfield (111) established by the Ames test that the mutagenic action of various policyclic aromatic hydrocarbons, aromatic amines, and some pesticides can be eliminated by oxidative degradation with ozone. However, the primary oxidation products of benzidine had stronger mutagenic action (111,112), though on further ozonization they were degraded to inactive products.

Spanggord (112) studied the ozonization of 30 organic compounds in high concentrations to obtain large concentrations of intermediate products. The mutagenicity of these was then investigated in the Ames test (113).

The compounds in question were 2,4-dinitrotoluene, diphenylhydrazine, acetic acid, aroclor 1254, glucose, urea, cholesterol, benzidine, glycine, cysteine, benzene, thymine, caffeine, diethylamine, phenol, hydroquinone, glycerol, and nitrilotriacetic acid in up to 1% solutions. Only the ozonized solutions of phenol, 1,1-diphenylhydrazine, nitrilotriacetic acid, benzidine, and ethanol were shown to be mutagenic after ozonization. A selection of the compounds used is listed in Table 6.

TABLE 6 Ozonization of organic substances after Spanggord (112) and Simmons (113)

Compounds	Concentration	Ozone amount	Degradation	Mutagenicity before O_3	Mutagenicity after O_3
2,4-dinitrotoluene	80 ppm	1.7 g	55 %	--	--
Oleic acid	99 ppm	2.55 g	100 %	--	--
Acetic acid	1263 ppm	37,2 g	3.5 %	--	--
Glycine	11900 ppm	9,8 g	22 %	--	--
Ethanol	7759 ppm	55,8 g	74 %	--	+
Benzidine dihydrochloride	4830 ppm	2,25 g	64 %	--	+
Phenol	9140 ppm	6.97 g	41 %		+

Salicylic acid

Mallevialle (52) established in the ozonization of salicylic acid (100 - 200 mg/l) with degradation of the starting compound an increase of the extinction at 420 nm, which, after reaching a maximum fell to zero with the elimination of the salicylic acid. Thin-layer chromatography revealed the presence of other phenolic oxidation products not identified more closely.

Phenols

Hillis (61) investigated the degradation of various substituted phenols (30 mg/l) at pH 4-10. It was found that not until pH 10 did the degradation proceed twice as rapidly as at pH 4 and 7. To achieve a degradation below 0.1 mg/l the same ozonization time was necessary in all cases.

Dore (114) found that during the ozonization of aminophenols, nitrophenols, and halophenols and of dichlorophenoxyacetic acid (25 mg/l) UV-active oxidation products were formed in the first phase of the reaction. The extinctions of the new absorption bands pass through a maximum and finally fall to zero after 100% degradation of the starting compound.

Bauch (115) was able to identify qualitatively the following oxidation products in the ozonization of cresol, chlorophenol, and xylenol (3.8 g/200 ml): glyoxylic acid, acetic acid, propionic acid, maleic acid, glycolic acid, oxalic acid, CO_2, and HCl. The degradation rate was independent of the pH.

2,4,5-Trichlorophenoxyacetic acid ($c=10^{-4}$M) was oxidized by ozone to chloride, glycolic acid, oxalic acid, glyoxylic acid, and dichloromaleic acid (116). The oxidation products were determined quantitatively.

The unidentified oxidation products of nitrophenols and phenol were shown in the mouse test to be non-toxic (117, 118).

The reactions of phenol with ozone have so far been studied in the greatest detail. Several working groups have determined the decrease of the phenol in the course of ozonization (119-122). The results on the pH-dependence reveal that the oxidation takes place more rapidly at pH 10-11 and the ozone consumption is only half of that in the acid region (119) (Table 7). Eisenhauer (123-125), in the ozonization of

TABLE 7 Ozonization of phenols

Compounds	Ozone consumption until the phenols fall below the detection level	Ref.
Salicylic acid	3 moles O_3/1 mole acid	52
Phenolsulphonic acid Chlorophenols Aminophenols Nitrophenols Cresol Xylenol Naphthol	4.9 moles O_3/mole phenol (mean value)	61
Amino, nitro, and halophenols	5 moles O_3/mole phenol	114
Cresol, chlorophenol, xylenol	5.5 moles O_3/mole phenol	115
Chlorophenols	3-4.5 moles O_3/mole phenol (pH 5)	72
Dichlorobenzene	6 moles O_3/mole benzene	88
Phenol	4 moles O_3/mole phenol (pH 7) 2 moles O_3/mole phenol (pH 12)	119
Phenol	6 moles O_3/mole phenol 4-6 moles O_3/mole phenol	122 127

phenol solutions (50 mg/l), obtained practically the same rate of degradation until pH 9. Only at pH 11 was the degradation rate doubled. Pyrocatechol quantitatively and o-quinone qualitatively were identified as the first oxidation products.

Reissaus (35) identified oxalic acid qualitatively as one of the oxidation products. Casalini (126) ozonized phenol solutions with 500, 1400, and 5000 mg/l in a 3.75-litre container (ozone doses 23/26 mg O_3/min) for 40 h at pH 3-11. Pyrocatechol and hydroquinone were determined together quantitatively as the oxidation products and maleic acid, formic acid, glyoxal, formaldehyde, and oxalic acid were found to be present. Gould (127) studied phenol solutions (90 mg/l, pH 7.7) ozonized for periods of up to 30 min (ozone dose 72 mg O_3/min). Pyrocatechol, hydroquinone, glyoxylic acid, and oxalic acid were recorded quantitatively as oxidation products during the ozonization. On the basis of the carbon balance these are the only reaction products. On the other hand, Niki (128) found formic acid to be one of the main products of the ozonization of phenol. In this case 57 mg of phenol in 100 ml of water were treated with only 5.8 mg O_3/min for 180 min. Muconic acid, muconaldehyde, maleic aldehyde, glyoxylic acid, glyoxal, and oxalic acid were identified quantitatively as further oxidation products, making up 100% of the TOC.

Substituted aromatics and their oxidation products

The different results obtained by the various working groups can be explained by their use of different reaction conditions such as the initial concentration, dose of ozone, ozonization time, pH, and reaction volumes or reaction vessels. Furthermore, the different rate constants are responsible for the formation and concentration distribution of the oxidation products. Fig. 6 shows that the unsaturated aliphatic carboxylic acids are degraded more rapidly than the substituted aromatics. Therefore, after their formation, they can be immediately oxidized further in competitive reactions with the starting compounds.

For example, with low ozone doses and high initial concentrations the chances of being able to isolate unsaturated aliphatic carboxylic acids such as fumaric or muconic as the oxidation products are higher than in the case of large ozone doses and low initial concentrations; this can be seen on the example of the ozonization of phenol under various conditions (126-128). For a better understanding of the

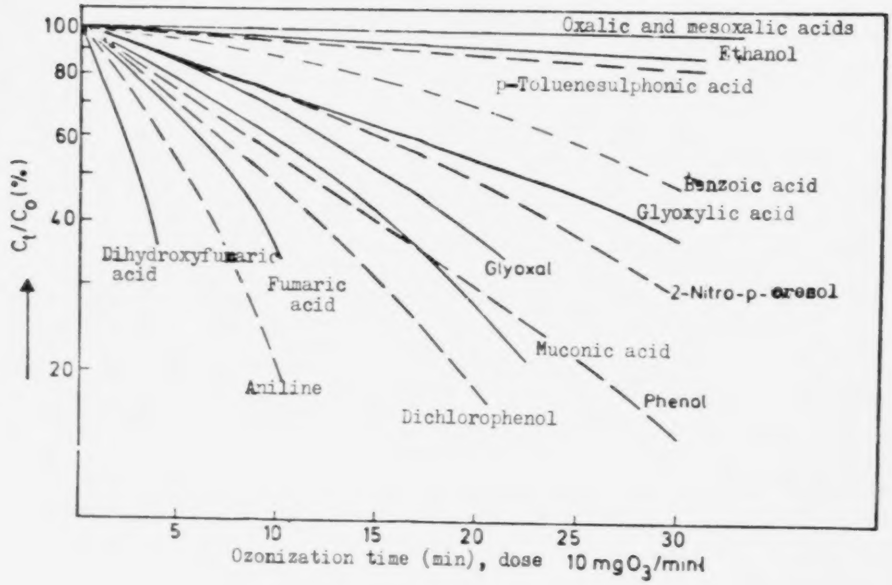


Fig. 6 Degradation of aliphatic and aromatic compounds in the ozonization of aqueous solutions, ozone dose 10 mg O_3/min l

c_t = concentration at ozonization time t

c_o = initial concentration 1 mmole/l

course of the reaction during ozonization it is necessary to know the rate constants. Hoigné has contributed much to this problem (129,130). It appears that in the acid range the ozone molecule is directly responsible for the oxidation reactions, while in the basic range the decomposition product of ozone formed by OH^- ions, the OH radical, initiates the oxidation by addition and abstraction reactions.

In the light of the work presented, the ozonization of substituted aromatic substances can be represented as follows. 2-6 moles of ozone are necessary for the elimination of 1 mole of the aromatic initially present (Table 7). In the initial phase of the reaction (up to about 50% degradation) an increasing coloration (pink or yellow) of the solution is observed or a new UV extinction is measured. The colour intensity and/or the UV extinction reaches a maximum on elimination of the starting compound and then falls to zero (52, 114, 116, 119, 128, 133, 134). These observations indicate that the first step in the ozonization of substituted aromatic substances need not be the spontaneous ring opening but that the primary oxidation products - it is not known to what extent they are formed - have an aromatic character or a six-membered ring structure. These primary oxidation products could be, for example, hydroxylated or quinoid compounds, such as have so far only been identified in the ozonization of phenol (as quinone, hydroquinone, and pyrocatechol)(123, 126-128).

If ring cleavage then occurs by further attack of ozone or OH radicals, muconic acid derivatives can be formed, which are transformed via maleic or fumaric acid derivatives into carbonyl and/or carboxyl compounds with one to three carbon atoms.

The course of these subsequent reactions has been studied on model compounds such as muconic, maleic, and fumaric acids and their oxidation products (54, 131, 132). All the compounds (Table 8) could be followed quantitatively, so that reaction mechanisms may be proposed.

The oxidation products of the aliphatic model substances were also found in the ozonization of substituted aromatics and phenols (Fig. 7). This indicates that after ring cleavage further oxidation takes place via muconic or fumaric acid derivatives.

After ring cleavage the substituents are converted into their mineralized form (54, 72). The detection of dichloromaleic acid (Fig. 7) (116) shows that the hetero-groups do not

TABLE 8 Ozonization of aliphatic carbonyl and carboxylic compounds.

Initial concentration 1 mmole/l; ozone dose 10 mg O_3/min l; ozonization time 20-180 min; pH 3

Compounds	Oxidation products	Ref.
trans,trans-Muconic acid	Fumaraldehyde, glyoxal, glyoxylic acid, oxalic acid, formic acid, CO_2, H_2O_2	132
Formic acid	CO_2, H_2O	131
Glyoxylic acid	Oxalic acid, CO_2	
Maleic acid	Formic acid, glyoxylic acid, oxalic acid, CO_2	
Fumaric acid	Formic acid, glyoxylic acid, oxalic acid, mesoxalic acid aldehyde, mesoxalic acid CO_2	
Glyoxal	Glyoxylic acid, oxalic acid, CO_2	54
Tartronic acid	Mesoxalic acid	"
Malonic acid	Tartronic acid, mesoxalic acid, CO_2, H_2O_2	"
Dihydroxyfumaric acid	Oxalic acid, hydroxytartaric acid, CO_2	"
Oxaloacetic acid	Formic acid, glyoxylic acid, oxalic acid, mesoxalic acid, CO_2	"

always hydrolyse spontaneously after ring cleavage and are not always converted completely into the inorganic form. Depending on the substituent, many further aliphatic oxidation products that contain hetero-groups are possible, but so far they have not been identified. Even in the case of p-toluenesulphonic acid (135), 2-nitro-p-cresol (135), and 4-chloro-o-cresol (54) so far only the oxidation products given in Fig. 7 could sometimes be followed quantitatively in the course of the ozonization (Table 9).

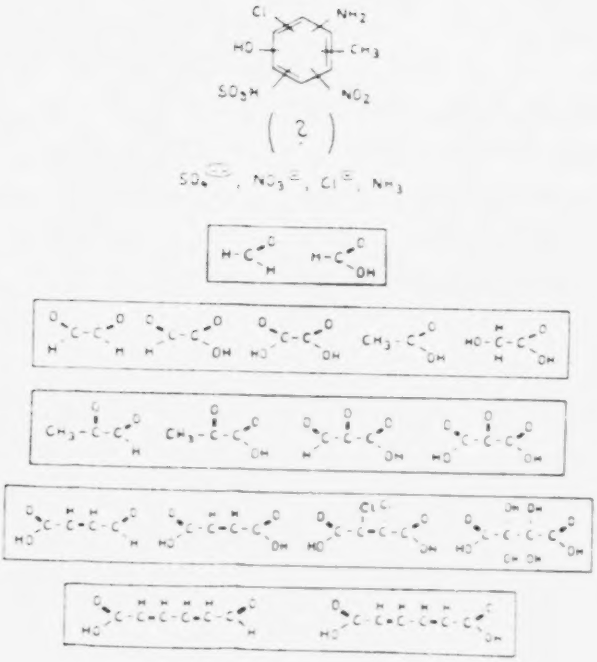


Fig. 7

Oxidation products identified so far in the ozonization of substituted aromatic substances

By comparing the TOC calculated from the measured products with the directly determined TOC (Figs. 8-10), it can be seen that at the beginning of the ozonization only a small part of the oxidation products (24-60%) was included. The maximum of the deficit lies at 90-100% elimination of the starting compounds. At this time 1.5 - 5 mg of O_3 are used up per mg of the initial C-value. Only after higher ozone consumption can 60 - 80% of the oxidation products be detected quantitatively. As mentioned previously, the still unidentified products after 90% elimination of the starting compound may be compounds with a 6-membered ring structure.

The first attempts to characterize these products showed that up to 90% degradation of the initial compounds the BOD_5/COD ratio was 0.1 and lower (134). The ozonization of aniline may be quoted as an example (Fig. 11). After 90% degradation the solution has a reddish colour. The BOD_5/COD of 0.64 for the non-ozonized solution falls to 0.01 after

TABLE 9 Ozonization of substituted aromatic substances (pH 5 - 2.5).

Initial concentration 1 mmole/l; ozone dose 24 mg O_3 min 1 for the p-toluenesulphonic acid; 10 mg O_3/min 1 in all other cases.

Compounds	Oxidation products	Fraction of products in TOC, %, after 90% degradation	
		for the starting compound	after higher ozone dose
p-Toluenesulphonic acid	Methylglyoxal, acetic acid, pyruvic acid, formic acid, oxalic acid, CO_2, H_2O_2, H_2SO_4	64% after 5.7 mg O_3/mg C 9.9 mole O_3/mole PTA	79% after 8 mg O_3/mg C
2-Nitro-p-cresol	Methylglyoxal, glyoxylic acid, acetic acid, pyruvic acid, formic acid, oxalic acid, CO_2, H_2O_2, HNO_3	38% after 2.5 mg O_3/mg C 4.4 mole O_3/mole NC	68% after 6.9 mg O_3/mg C
4-Chloro-o-cresol	Methylglyoxal, acetic acid, pyruvic acid, formic acid, oxalic acid, CO_2, HCl, H_2O_2	24% after 1.3 mg O_3/mg C 2.3 mole O_3/mole CC	65% after 3 mg O_3/mg C

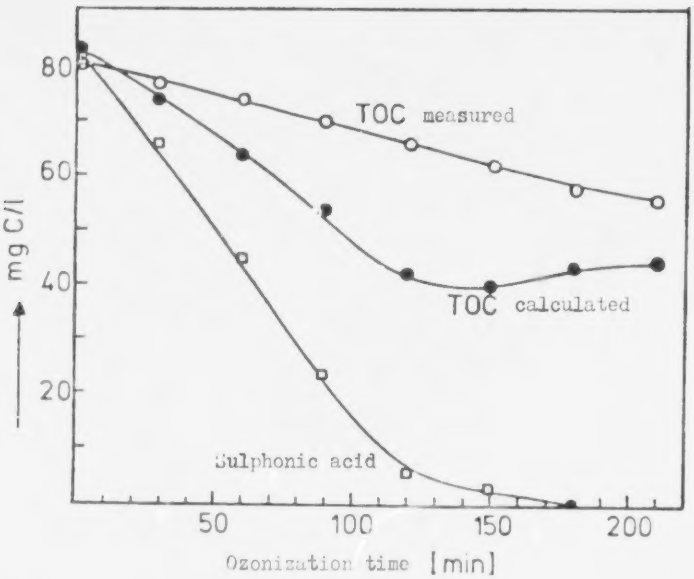


Fig. 8 Ozonization of p-toluenesulphonic acid, carbon balance

c = 1 mmole/l; ozone dose 24 mg O_3/min l; pH 3

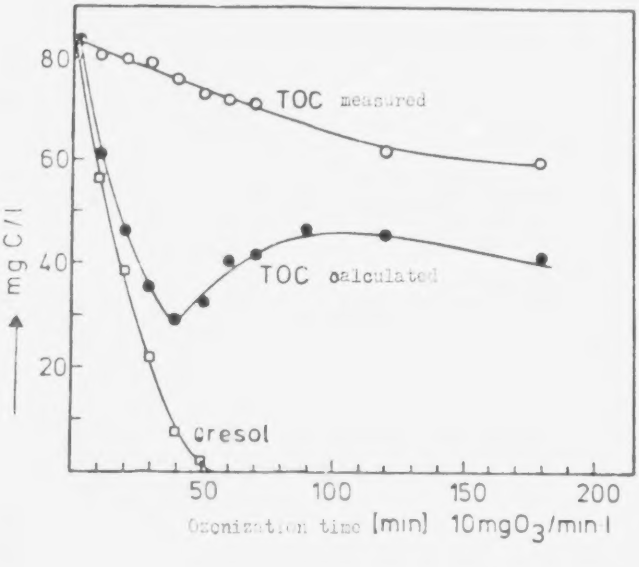


Fig. 9 Ozonization of 2-nitro-p-cresol, carbon balance

c = 1 mmole/l; ozone dose 10 mg O_3/min; pH 5.5

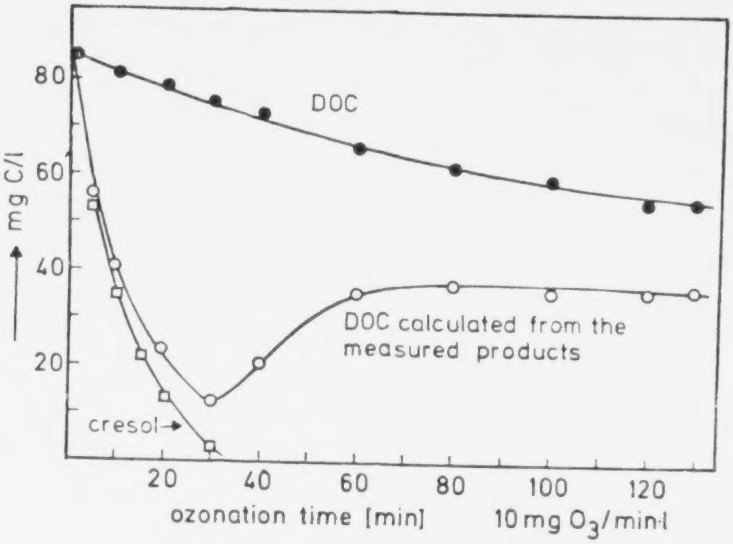


Fig. 10 Ozonization of 4-chloro-o-cresol, carbon balance c = 1 mmole/l; ozone dose 10 mg O_3/min l; pH 5.5

10 min of ozonization (Fig. 11). After larger additions of ozone (6 mg O_3/mg C) the solution again becomes colourless. In this region the oxidation products formed are also better degradable biologically.

It can be seen from the example of phenols and substituted aromatics that some of the reaction mechanisms postulated for ozonization could only be confirmed by clarifying the oxidation products and particularly by their quantitative determination. In the light of the material balances obtained the existence of primary oxidation products may also be proved, though up to now little is known about their identity and their properties. Of the remaining classes of substances it may be said that so far only the reactions of ozone with unsaturated aliphatic carboxylic acids and aliphatic alcohols

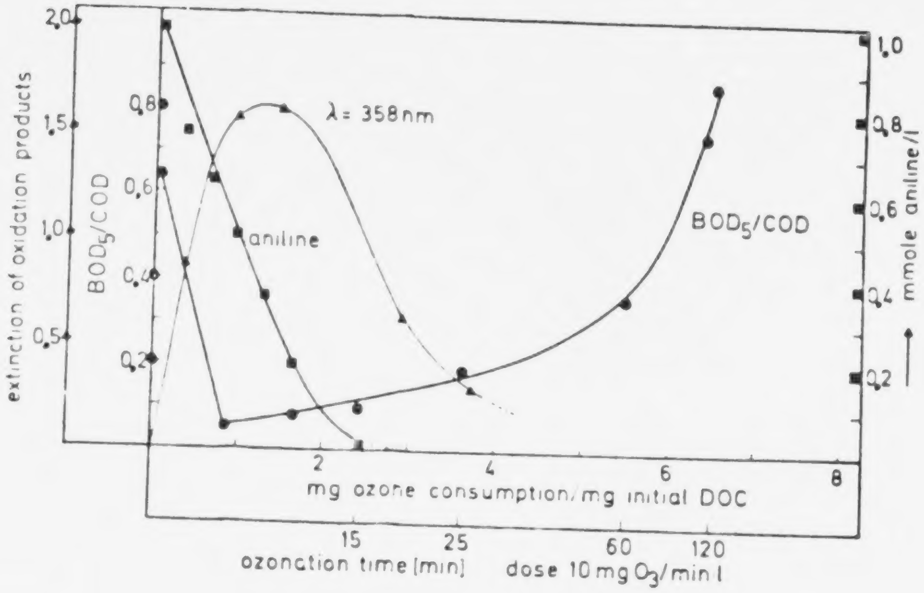


Fig. 11 Ozonization of aniline, biological degradability of the oxidation products in dependence on the ozonization time

c = 1 mmole/l; ozone dose 10 mg O_3/min l; pH 6

and carbonyl compounds have been studied in any detail. As regards the compounds of other substance classes, so far there are only indications of their possible degradability. Even if the determination of the oxidation products is problematic because of the complicated composition of the ozonized solutions, one property should be checked, namely the toxicity. Little is yet known about this and more detailed work is required.

(1) KURZMANN, G.E.
Das indirekte Ozondruckverfahren
Wasser-Luft-Betrieb 7 (1963), 11

(2) BREDTMANN, M.
Ozonausnutzung durch Anwendung des Belüftungsprinzips
gwf-Wasser/Abwasser 115 (1974), 326

(3) SCHAEFER, R.J.
Ozone sewage treatment apparatus
United States Patent 3, 680, 704, Aug. 1 (1972)
U.S. Cl. 210/218

(4) TREJTNAR, J.
Ozonizer for treating water
Czechoslovakian Patent 139879, C 02 b 1/38

(5) BLATTER, M.
Verfahren und Einrichtungen zur Aufbereitung von
Detergentien enthaltendem Abwasser mittels Ozon
Schweizer Patentschrift 521292 C 02 c 5/04, 15. Mai 1972

(6) BOWERS, A., NETZER, A., NORMAN, J.D.
Ozonation of waste water - some technical and
economic aspects
The Can. J. of Chem. Eng. 51 (1973), 332

(7) MASSCHELEIN, W., FRANSELOT, G., GENOT, J.
Techniques for dispersing and dissolving ozone in
water
Water and Sewage Works, Dec. (1975), 57

(8) NEBEL, C., UNANGST, P.C., GOTTSCHLING, R.
An evaluation of various mixing devices for dispersing
ozone in water
Water and Sewage Works 120 (1973), R-6

(9) ROSEN, H.M.
Use of ozone and oxygen in advanced waste water
treatment
J. WPCF 45 (1973), 2521

(10) ZAITSEV, V.A., KOLDASHEV, A.N. et al.
Contact unit for ozone treatment of waste water
designed by Nickhimmash
The Soviet Chemical Industry 6 (1974), 10, 653

(11) HEIST, J.A.
Ozone oxidation of waste water contaminants
A Literature Review
AIChE Symposium Series Water 1973, 70 (1973), 136, 456

(12) MAJUMDAR, S.B., CHECKLER, W.H., SPROUEL, O.I.
A physical and mathematical model of mass transfer and reaction kinetics of ozonation
AIChE Symposium Series 73 (1977), 166, 188

(13) RICHARDS, D.A., FLEISCHMANN, M., EBERSOLD, L.P.
Mass transfer coefficients for the ozone-water system
AIChE Symposium Series 73 (1977), 166, 213

(14) HOATHER, R.C.
Some experimental observations on the solubility of ozone and the ozonation of a variety of waters
J. of the Inst. of Water Engineers London 2 (1948), 358

(15) STUMM, W.
The solubility of ozone in aqueous solution
Helv. Chim. Acta 37 (1954), 773

(16) KILPATRICK, M.L., HERRICK, C.C.
The decomposition of ozone in aqueous solution
J. Am. Chem. Soc. 78 (1956), 1784

(17) CZAPSKI, G., SAMUNI, A., YELIN, R.
The disappearance of ozone in alkaline solution
Israel Journal of Chemistry 6 (1968), 969

(18) HEWES, C.G., DAVISON, R.R.
Kinetics of ozone decomposition and reaction with organics in water
AIChE Journal 17 (1971), 141

(19) GORBENKO-GERMANOV, D.S., KOZLOWA, I.B.
Intermediate decomposition products of ozone in alkaline aqueous media investigated by ESR
Zhur. Fiz. Khim. 48 (1974), 1998

(20) KUO, C.H., WEN, K.Y. et al.
Absorption and decomposition of ozone in aqueous solutions
AIChE Symposium Series 73 (1977), 166, 230

(21) LEBOUT, H.
Fifty years of ozonation at Nice
Ozone Chemistry and Technology, Advances in Chemistry Series 21 (1959), 450

(22) KATZENELSON, E., KELTER, B., SHUVAL, H.I.
Inactivation of viruses and bacteria in water by use of ozone
J. AWWA 66 (1974), 725

(23) KATZENELSON, E., BIEDERMANN, N.
Disinfection of viruses in sewage by ozone
Water Research 10 (1976), 629

(24) KELLER, I.W., MORIN, R.A.
Ozone disinfection, pilot plant studies at Laconia, H.H.
J. AWWA 66 (1974), 730

(25) KINMAN, R.N.
Water and wastewater disinfection with ozone: A critical review
CRC Critical Reviews in Environm. Control 5 (1975), 141

(26) PERRIL, J., McCAMMON, J., CRONHOLM, L. et al.
Ozone disinfection and oxidation in a model ozone contacting reactor
AIChE Symposium Series 73 (1977), 166, 225

(27) HACKER, D.S., LOCKOWITZ, T.
Use of ozone in the disinfection of coliphage T-7 virus
AIChE Symposium Series 73 (1977), 166, 242

(28) FOCHTMANN, E.G., RICE, R.G., BROWNING, M.E.
Forum on ozone disinfection
International Ozone Institute Inc., Syracuse, New York (1977)

(29) MUDD, J.R., LEAVITT, R., ONGUN, A., McMANUS, T.T.
Reaction of ozone with amino acids and proteins
Atmosph. Environm. 3 (1969), 669

(30) MENZEL, B.
Oxidation of biologically active reducing substances by ozone
Arch. Environm. Health 23 (1971), 149

(31) SHUVAL, H.I.
Forschungsbericht 02 WA 71, Universität Jerusalem (1976)

(32) O'DONOVAN, D.C.
Treatment with ozone
J. AWWA 57 (1965), 1167

(33) HOPF, W.
Zur Wasseraufbereitung mit Ozon und Aktivkohle
gwf-Wasser/Abwasser 111 (1970), 83-92/156-164

(34) HOLLUTA, J.
Ozon in der Wasserchemie
gwf-Wasser/Abwasser 104 (1963), 129

(35) REISSAUS K., RUMMEL, R.
Wasseraufbereitung mit Ozon bei der Trinkwasserschönung
Fortschr. in der Wasserchemie 6 (1967), 139

(36) KURZMANN, G.
Ozon in der Wasseraufbereitungstechnik
Wasser-Luft-Betrieb 8 (1959), 204

(37) MELNYK, P.B., JUDKINS, D., NETZER, A.
An ozone reactor for color removal from
pulp bleachery wastes
Tappi 60 (1977), 3, 97

(38) BAUMANN, H.D., LUTZ, L.R.
Ozonation of a kraft mill effluent
Tappi 57 (1974), 116

(39) MEIJERS, A.P.
Quality aspects of ozonisation
Water Research 11 (1977), 647

(40) MÖRGELI, B.
Chemisch-physikalische Verfahren zur Reinigung von
Abwässern in der Textilveredelungsindustrie
Melliand Textilberichte 56 (1975), 78

(41) PALIN, A.T.
The ozonation of water with special reference to
colour removal
Water and Water Engineering, July (1953), 271

(42) CAMPBELL, R.M.
The use of ozone in the treatment of loch turret water
J. of the Inst. of Water Engineers 17 (1963), 333

(43) SNIDER, E.H., PORTER, J.J.
Ozone treatment of dye waste
J. WPCF 46 (1974), 886

(44) FURGASON, R.R., HARDING, H.L., SMITH, M.A.
Ozone treatment of waste effluent
Research Technical Completion Report OWRR
Project No. A - 037 - IDA - April (1973)

(45) FURGASON, R.R. et al.
Ozone treatment of kraft mill effluent
AIChE Symposium Series 70 (1974), 139, 32

(46) SUZUKI, I.
Study on ozone treatment of water-soluble polymers
I. Ozone degradation of polyethylene glycol in water
J. of Applied Polymer Science 20 (1976), 593

(47) MAIER, D., KURZ, R.
Untersuchungen zur Optimierung der Ozonanwendung
bei der Aufbereitung von Seewasser
Internat. Symposium Ozon und Wasser Berlin (1977), 211

(48) SONTHEIMER, H., WÖLFEL, P., SARFERT, E.
Improved biological decomposition of organic substances
contained in biologically-cleansed sewage after ozonation
Proceedings 3rd Symposium of the Internat. Ozone Institute
4-6 May Paris (1977)

(49) GIURGIUS, W., COOPER, T., HARRIS, J., UNGAR, A.
Improved performance of activated carbon by pre-ozonation
J. WPCF 50 (1978), 308

(50) GILBERT, E.
Über die Wirkung von Ozon auf hochmolekulare Wasserinhaltsstoffe
To be published Vom Wasser (1978)

(51) KOPPE, P., HERKELMANN, H., SEBESTA, G.
Die Behandlung des Abwassers einer Zellstoff- und
Papierfabrik mittels Ozon und Belebtschlammverfahren
Vom Wasser 46 (1976), 221

(52) MALLEVIALLE, J.
Action de l'ozone dans le dégradation des composés
phenoliques simples et polymérisés. Application aux
matières humiques contenues dans les eaux
Techniques et sciences municipales et revue l'eau
70 (1975), 107

(53) MALLEVIALLE, LAVAL, Y., LEFEBRE, M., ROUSSEAU, C.
The degradation of humic substances in water by
various oxidation agents
Proceedings Ozone/Chlorine Dioxide Oxidation Products
of Organic Matter
Cincinnati, Ohio, Nov. (1976), 189

(54) GILBERT, E.
Reactions of ozone with organic compounds in dilute
aqueous solution, identification of their oxidation
products
Proceedings Ozone/Chlorine Dioxide Oxidation Products
of Organic Matter
Cincinnati, Ohio, Nov. (1976), 227

(55) MEIJERS, A.P.
Entfernung von organischen Wasserinhaltsstoffen,
Färbung sowie Geschmacksstoffen durch Ozon
Internationales Symposium Ozon und Wasser Berlin
(1977), 233

(56) HALFON A. et al.
Organic residue removal from waste waters by
oxidation with ozone
Division of Water, Air and Waste Chemistry, Am. Chem.
Soc., Atlantic City meeting Sept. (1968), 32

(57) KWIE, W.W.
Ozone treats waste streams from polymer plant
Water and Sewage Works 116 (1969), 74

(58) GARDINER, D.K., MONTGOMERY, H.A.C.
The treatment of sewage effluent with ozone
Water and Waste Treatment Sept./Oct. (1968), 92

(59) BOBER, T.W., DAGON, T.J.
Ozonation of photographic processing wastes
J. WPCF 47 (1975), 2114

(60) WACHS, A., NARKIS, N., SCHNEIDER, M.
Organic matter removal from effluent by lime treatment,
ozonation and biologically extended activated carbon
treatment
3rd Symposium of the Internat. Ozone Inst. 4-6 May
Paris (1977)

(61) HILLIS, M.R.
The treatment of phenolic wastes by ozone
Organic matter removal from effluent by lime treatment,
ozonation and biologically extended activated carbon
treatment
3rd Symposium of the Internat. Ozone Inst. 4-6 May
Paris (1977)

(62) WALTER, R.H., SHERMAN, R.M.
Ozonation of lactic and fermentation effluent
J. WPCF 46 (1974), 1800

(63) WYNN, C.S., KIRK, B.S., NcNABNEY, R.
Pilot plant for tertiary treatment of waste water
with ozone. Environmental Protection Technology
Series EPA - R2 - 73 - 146 Jan. (1973)

(64) MALLEVIALLE, J.
Ozonation des substances de type humique dans les
eaux
Proceedings of the 2nd Internat. Symp. on Ozone
Technology, Montreal/Canada May (1975), 262

(65) MELNYK, P.B., NETZER, A.
Reactions of ozone with chromogenic lignins in pulp and paper mill waste water
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 321

(66) NEBEL, C., STUBER, L.M.
Ozone decolorization of secondary dye laden effluents
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 336

(67) DUFORT, J., JONES, J.P.
Direct physicochemical treatment with ozone
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 545

(68) NETZER, A., BESZEDITS, S., WILKINSON, P., MIYAMOTO, H.K.
Treatment of dye wastes by ozonation
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 359

(69) DAVIS, G.M. et al.
Ozonation of waste waters from organic chemicals manufacture
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 421

(70) SMITH, M.A., FURGASON, R.R.
Use of ozone in the treatment of kraft pulp mill liquid wastes
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 309

(71) McCARTHY, J.M.
The influence of particle size on oxidation of total, soluble and particulate municipal waste water components by ozone
Proceedings of the 2nd Internat. Symp. on Ozone Technology, Montreal/Canada May (1975), 522

(72) GILBERT, E.
Über den Abbau von organischen Schadstoffen im Wasser durch Ozon
Vom Wasser 43 (1974), 275

(73) ROOK, J.J.
Haloforms in drinking water
J. AWWA 68 (1976), 168

(74) SANDER, R., KÜHN, W., SONTHEIMER, H.
Untersuchungen zur Umsetzung von Chlor mit Huminsubstanzen
Z. f. Wasser und Abwasser-Forschung 10 (1977), 155

(75) MAIER, D., MÄCKLE, H.
Wirkung von Chlor auf natürliche und ozonte organische Wasserinhaltsstoffe
Vom Wasser 47 (1976), 379

(76) HUBBS, S.A.
The oxidation of haloforms and haloform precursors utilizing ozone
Proceedings Ozone/Chlorine Dioxide, Oxidation Products of Organic Material, Cincinnati, Ohio, Nov. 17-19 (1976), 200

(77) LAWRENCE, J.
The oxidation of some haloform precursors with ozone
3rd Symp. of the Internat. Ozone Inst. 4-6 May Paris (1977)

(78) SCHALEKAMP, M.
Die Erfahrungen mit Ozon in der Schweiz, speziell hinsichtlich der Veränderung von hygienisch bedenklichen Inhaltsstoffen
Internat. Symp. Ozon und Wasser Berlin (1977), 31

(79) BLOCK, J.C., MORLOT, M., FOLIQUET, J.M.
Problèmes liés a l'evolution du caractère d'oxydabilité de certains corps organiques présents dans l'eau traitée par l'ozone
Techniques et Sciences Municipales. L'eau 71 1 (1976), 29

(80) BUYDENS, R.
L'ozonation et ses repercussions sur le mode d'epuration des eaux de rivière
La Tribune du Cebedeau 23 (1970), 286, 319

(81) KÜHN, W., SONTHEIMER, H., STIEGLITZ, L., MAIER, D., Kurz, R.
Use of ozone and chlorine in water utilities in the Federal Republic of Germany
J. AWWA 70 (1978), 6, 326-331

(82) NAIMIE, G., AXT, G., SONTHEIMER, H.
Zur katalytischen Beeinflussung der Oxidation von organischen Wasserinhaltsstoffen
Vom Wasser 37 (1970), 98

(83) REICHERTER, U.F.
Untersuchungen über die Anwendung von Ozon bei der Wasser- und Abwasserreinigung
Dissertation, Fakultät für Chemieingenieurwesen, Universität Karlsruhe (1973)

(84) EICHELSDÖRFER, D., v. HARPE, Th.
Einwirkung von Ozon auf Harnstoff im Hinblick auf die Badewasseraufbereitung
Vom Wasser 37 (1970), 73

(85) DOBINSON, F.
Ozonisation of malonic acid in aqueous solution
Chemistry and Industry, June 27 (1959), 853

(86) BLACK, W.T., COOK, G.A.
Production of glyoxalic acid
I. and EC Product Research and Development 5 (1966), 4, 351

(87) SHAPIRO R.H. et al.
Ozonization products from caffeine in aqueous solution
Proceedings Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, Cincinnati, Ohio (1976), 284

(88) SHARIFOV, R.R., BONDAREVA, N.I., MAMED-YAROVA, L.A.
Oxidation von Dichlorbenzol durch Ozon
Azerbaidzhanskii khimicheskii zhurnal (1973), 4, 124 (Russ.)

(89) WALTER, R.H., SHERMAN, R.M.
Reduction in chemical oxygen demand of ozonated sugar solutions by charcoal
J. of Food Science 43 (1978), 404

(90) KRAUSE, H., HEPP, H., KLUGER, W.
Versuche zur Zerstörung von Komplex- und Chelatbildnern in radioaktiven Abwässern durch Oxidation
Kernforschungszentrum Karlsruhe KFK 287, Sept. 1964

(91) KUO, C.H., WEN, C.P.
Ozonizations of formic acid, formaldehyde and methanol in aqueous solutions
AIChE Symposium Series 166, 73 (1977), 272

(91a) KRASNOV, B.P., PAKUL, D.L., KIRILOVA, T.V.
Use of ozone for the treatment of industrial waste waters
Int. Chem. Engin. 14 (1974), 4, 747

(92) PAKUL, D.L., KRASNOV, B.P., SAZHINA, A.M.
Oxidation of alcohols in dilute aqueous solutions by ozone
Zhurnal Prikladnoi Khimii 47 (1974), 1, 36

(93) KUO, P.K., CHIAN, E.S.K., CHANG, B.J.
Identification of end products resulting from ozonation and chlorination of organic compounds commonly found in water
Environmental Science & Techn. 11 (1977), 1177

(94) GILBERT, E.
Chemische Vorgänge bei der Ozonanwendung
Int. Symp. Ozon und Wasser Berlin 77
Colloquium Verlag Otto H. Hess, Berlin (1977), 277

(95) BUESCHER, C.A., RYCKMAN, D.W.
Reduction of foaming of ABS by ozonation
Proceedings 16th Industrial Waste Conference,
Purdue University, Lafayette, Indiana (1961), 251

(96) EVANS, F.L., RYCKMAN, D.W.
Ozonated treatment of wastes containing ABS
Proceedings 16th Industrial Waste Conference
Purdue University, Lafayette, Indiana (1963), 141

(97) KANDZAS, P.F., MOKINA, A.A.
Verwendung von Ozon zur Reinigung von Abwässern von synthetischen oberflächenaktiven Anionen-Substanzen
Ochistka proizvodstvennyk stochnykh vod 4 (1969), 76-86
(Russ.)

(98) JOY, P., GILBERT, E., EBERLE, S.H.
Untersuchungen über die Wirkung des Ozons auf Alkylbenzolsulfonsäure und Waschmittel in wässriger Lösung
"Organische Verunreinigungen in der Umwelt" Hrsg.
K. Aurand, Berlin (1978), 164
ISBN 3-503-01713-5

(99) REICHERT, J.
Untersuchungen zur Eliminierung kanzerogener aromatischer Polyzyklen in der Trinkwasseraufbereitung unter besonderer Berücksichtigung des Ozons
gwf-Wasser/Abwasser 110 (1969), 18, 477

(100) GOMELLA, C.
Ozone practices in France
J. AWWA 64 (1972), 39

(101) HOFFMANN, I., EICHELSDÖRFER, D.
Zur Ozoneinwirkung auf Pestizide der Chlorkohlenwasserstoffgruppe im Wasser
Vom Wasser 38 (1971), 198

(102) MÖRGELI, B.
Entfernung von Pestiziden aus Trinkwasser
Gas, Wasser, Abwasser 52 (1972), 142

(103) ROBECK, G.G. et al.
Effectiveness of water treatment processes in pesticides removal
J. AWWA 57 (1965), 181

(104) ROSS, W.R., v. LEEUWEN, J., GRABOW, W.O.K.
Studies on disinfection and chemical oxidation with ozone and chlorine in water reclamation
Proceedings 2nd Int. Symp. on Ozone Techn.
Montreal, Canada (1975), 497

(105) BROWER, G.R.
Ozonation reactions of selected pesticides for water pollution abatement
Dissertation Abstracts B (1967), 28, 722-B

(106) RICHARD, Y., BRENER, L.
Organic materials produced upon ozonization of water
Proceedings Ozone/Chlorine Dioxide Oxidation Products of Organic Materials. Cincinnati, Ohio, Nov. (1976), 169

(107) LAPLANCHE, A., MARTIN, G., RICHARD, Y.
Etude de la degradation des posticides par l'ozone: cas du parathion
La Tribune du Cebedeau 27 (1974), 22

(108) LAPLANCHE, A., MARTIN, G., RICHARD, Y.
Ozonation d'une eau polluée par du parathion
T.S.M. l'Eau 7 (1974), 407

(109) DAGON, T.J.
Photographic processing effluent control
J. of Appl. Photogr. Eng. 4 (1978), 2, 62

(110) BAUCH, H., BURCHARD, H.
Über Versuche, stark riechende oder schädliche Abwässer mit Ozon zu verbessern
Wasser-Luft-Betrieb 14 (1970), 134

(111) CAULFIELD, M.J.
Kinetic studies of the ozonation of carcinogens and mutagens as monitored by biological assay; Univ.Notre Dame,
Dissertation Abstracts Internat. B 38 (1978), 10, 4644-4645

(112) SPANGGORD, R.J., McCLURG, V.J.
Ozone methods and ozone chemistry of selected organics in water
Proceedings Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, Cincinnati, Ohio (1976), 115

(113) SIMMON, V.F., ECKFORD, S.L., GRIFFIN, A.F.
Ozone methods and ozone chemistry of selected organics in water, 2. Mutagenic Assay
Proceedings Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, Cincinnati, Ohio (1976), 126

(114) DORE, M., LANGLAIS, B., LEGUBE, B.
Ozonation des phenols et des acides phenoxy-acetiques
Water Research 12 (1978), 413

(115) BAUCH, H., BURCHARD, B., ARSOVIC, M.
Ozon als oxidatives Abbaumittel für Phenole in wässrigen Lösungen
Gesundheits-Ingenieur 91 (1970), 9, 258

(116) STRUIF, B., WEIL, L., QUENTIN, K.E.
Verhalten herbizider Phenoxy-Alkan-Carbonsäuren bei der Wasseraufbereitung mit Ozon
Z. f. Wasser- und Abwasser-Forschung 11 (1978), 3, 4, 118

(117) KOROLEV, A.A., KORENKOV, V.N., ABINDER, A.A.
Problems of hygienic effectiveness of ozone treatment of water and sewage containing nitro compounds (Russ.)
Gigiena i sanitarja Moskva 11 (1974), 13

(118) KOROLEV, A.A., ABINDER, A.A., BOGDANOV, M.V.
Hygienic and toxicologic features of products of phenol destruction in ozone treatment of water
Gigiena i sanitarja Moskva 8 (1973), 6

(119) NIEGOWSKI, S.J.
Destruction of phenols by oxidation with ozone
Ind. and Eng. Chem. 45 (1953), 3, 632

(120) MATSUOKA, H. et al.
Ozone treatment of waste water
Report Mitsubishi Electric Co. 46 (1972), 552

(121) ANDERSON, G.L.
Ozonation of high levels of phenol in water
AIChE Symp. Series Water 73 (1976), 166, 265

(122) PASYNKIEWICZ, J., GROSSMAN, A., NAWARA, S.
Application of ozone in purification of drinking water containing phenols
Przemysl Chemiczny 47 (1968), 4, 231

(123) EISENHAUER, H.R.
Increased rate and efficiency of phenolic waste ozonation
J. WPCF 43 (1971), 200

(124) EISENHAUER, H.R.
The ozonation of phenolic waste
J. WPCF 40 (1968), 1887

(125) EISENHAUER, H.R.
Dephenolization by ozonolysis
Water Research 5 (1971), 467

(126) CASALINI, A., LEONI, A., SALVI, G.
Ozone purification of waste water containing phenol: Investigations of the oxidation mechanism
La Rivista dei Combustibili 31 (1977), 3, 92

(127) GOULD, J.P., WEBER, W.J.
Oxidation of phenols by ozone
J. WPCF 48 (1976), 47

(128) YAMAMOTO, Y., NIKI, E. et al.
Ozonation of organic compounds, II. Ozonation of phenol in water
Proceedings Ozone Technology Symp. Internat. Ozone Inst. May 23-25 (1978), Los Angeles, Cal.

(129) HOIGNE, J., BADER, H.
Ozonation of water: Selectivity and rate of oxidation of solutes
3rd Congress of the Internat. Ozone Inst. Paris, May 1977

(130) HOIGNE, J., BADER, H.
Ozone initiated oxidations of solutes in waste water: A reaction kinetic approach
Prog. Wat. Techn. 10 (1978), 657

(131) GILBERT, E.
Über die Wirkung von Ozon auf Maleinsäure, Fumarsäure und deren Oxidationsprodukte in wässriger Lösung
Z. Naturforsch. 32b (1977), 1308

(132) GILBERT, E.
Die Ozonung von Muconsäure
To be published

(133) ISHIZAKI, K., DOBBS, R.A., COHEN, J.M.
Ozonation of hazardous and toxic organic compounds in aqueous solution
Proceedings Ozone/Chlorine Dioxide Oxidation Products of Organic Material, Cincinnati, Ohio, Nov. (1976), 210

(134) GILBERT, E.
Investigations on the changes of biological degradability of single substances induced by ozonolysis
Ozone Technology Symp. May 1978, Los Angeles, Cal.

(135) GILBERT, E., JOY, P., EBERLE, S.H.
Ozonisierung von p-Toluolsulfonsäure und 2-Nitro-p-Kresol in wässriger Lösung
To be published

OZONE REQUIREMENT AND OXIDATION COMPETITION VALUES OF VARIOUS TYPES OF WATER FOR THE OXIDATION OF TRACE IMPURITIES

J. Hoigné and H. Bader

Many water constituents are oxidized in ozonization processes. In the last paper Gilbert showed corresponding case studies (1). The following fundamental questions thus arise: How complete are such oxidation reactions after a certain ozonization time ? Which materials are concentrated in the water as intermediate daughter products ?

The action of an ozonization process on the water constituents is essentially determined by two types of overlapping oxidation-initiating reactions (2-5):

- Direct reaction of the ozone
- Reactions of secondary oxidants formed in decomposition of the ozone ($OH^{\bullet}$ radical reaction).

Following a detailed outline of the parts played by the two types of reaction in earlier works (see e.g. (5)), the rest of the paper will be devoted mainly to a method of characterizing a water type with respect to the action of secondary oxidants. To this end we introduce the concepts "oxidation competition value of a water type" and "oxidation competition coefficient of a constituent".

1. Direct reaction of ozone

Ozone can react with many water constituents in direct reactions:

$$M + O_3 \xrightarrow{\eta \cdot k_{O_3}} M_x + \ldots\ldots$$

$$M_x + (1/\eta - 1)O_3 \longrightarrow M_{oxide}$$

Here M represents a specific water impurity and M_x an intermediate daughter product formed from it. Within the duration of the ozonization M_x reacts with further ozone molecules to form the daughter product M_{oxide}. Therefore, for the entire course of the reaction, $1/\eta$ molecules of O_3 are used up per converted material, i.e. η is a yield factor, $\Delta[M]/\Delta[O_3]$. The rate-determining step of the above reactions is by definition only the first step. Such direct reactions of ozone are of first order with respect to the ozone concentration and of first order with respect to the concentration of M (4-6), and the rate of elimination of a material M is:

$$-\frac{d[M]}{dt} = -\eta \cdot \frac{d[O_3]}{dt} = \eta \cdot k_{O_3} [O_3][M]$$

If the ozonization takes place in a batch-type or a plug-type reactor, it can be inferred from the above reaction scheme that the concentration of an individual water constituent decreases with increasing time of ozonization according to:

$$[M]_t / [M]_0 = e^{-t/\tau_M} \tag{1}$$

with

$$1/\tau_M = \eta \cdot k_{O_3} \cdot [\overline{O_3}] \tag{2}$$

where $[M]_t$, $[M]_o$ are the concentrations of the water constituent M at time t and at the beginning of the reaction,

t is the time of ozonization,

τ_M is the time constant of the reaction with respect to [M], and

k_{O_3} is the rate constant for the reaction of the ozone.

τ_M corresponds to the time of ozonization necessary in the presence of an ozone concentration $[\bar{O}_3]$ for an elimination of [M] to 37% (1/e), see Fig. 1. $1/\tau_M$ is a reaction rate. In a description of the disinfection process this is often denoted by μ. If M is an individual substance, i.e. not a sum parameter, τ becomes independent of the extent of the ozonization reaction, i.e. the logarithmic elimination curve shown in Fig. 1 becomes a straight line.

We measured the rate constants (k_{O_3}) for about 60 different substances, e.g. on the basis of the rate of decrease of the O_3 concentration as a function of the M concentration (6). With the measurement methods so tested the constants for further substances are easily determined if required. Fig. 2 gives some examples of these measurements. The results show that ozone is also an extremely selective oxidation agent in water: the k-values of even chemically similar materials can vary by orders of magnitude.

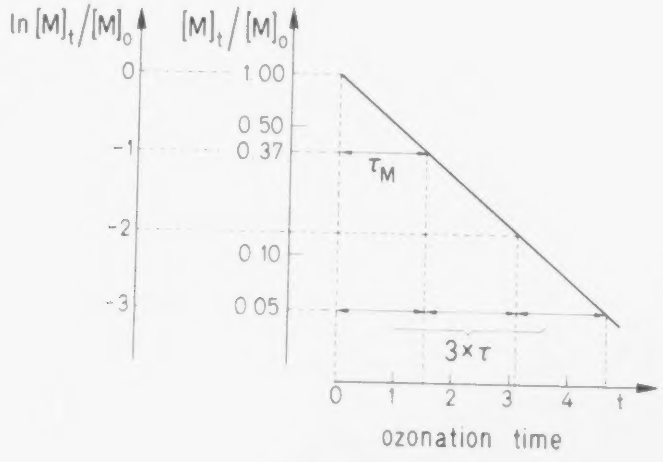


Fig. 1 Effect of the "direct O_3 reaction"
Logarithmic decrease of the relative concentration of a specified trace impurity M, plotted against the reaction time at a constant ozone concentration

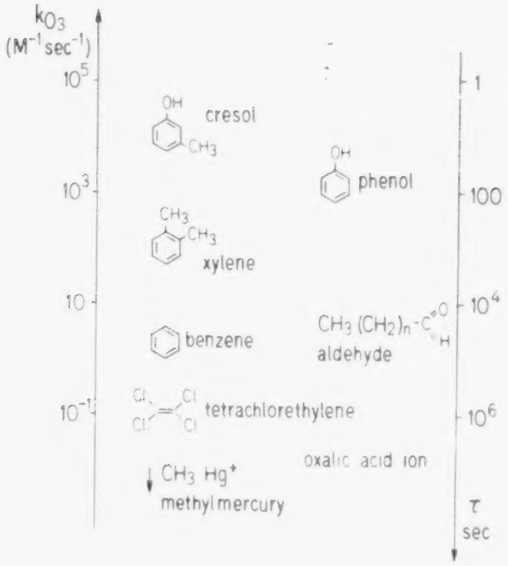


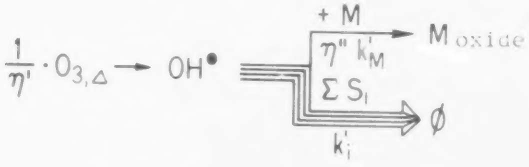
Fig. 2 Left scale: Examples of rate constants k_{O_3} (5,6)
Right scale: Time constants τ of the reaction, calculated according to equation 2 for $[O_3] = 10^{-5} M$ (ca. 0.5 g/m^3), $\eta = 1.0$

On the basis of the rate constants measured the time constant τ_M for the reaction of a constituent M can be calculated for a given ozone concentration. A corresponding time scale is set out in Fig. 2 on the right ordinate. It refers to a mean ozone concentration of 10^{-5} mole O_3/l (ca. 0.5 g/m^3) and to the assumption that the reaction yield is $\eta = 1.0$. At an ozone concentration 10 times as high this time scale would be compressed by a factor of 10. The illustration shows that cresol enters the reaction essentially within 10 sec. The concentration of phenol is reduced within about 100 sec to 37% of its starting value. (Other compounds too, known for the fact that they are easily chlorinated in chlorination of water, are readily degraded by ozone (6)).

In contrast to these readily oxidized substances, aldehydes, for example, which are concentrated in sea water as intermediate ozonization products, require really long ozonization times for further oxidation (5, 7, 8). Acids such as oxalic acids, which are also formed as oxidation products, have no chance of being mineralized further by the direct ozone reaction, even when the ozonization is continued for hours. Compounds such as methylmercury and tetrachloroethylene (9, 10) also hardly react by the "direct ozone reaction".

2. Oxidations via secondarily formed oxidants

In the ozonization of water the decomposition products of ozone, i.e. secondarily formed oxidants, are also available for oxidation of any trace impurities: depending on the water, a part of the ozone, $O_{3,\Delta}$, is decomposed. This part increases with increasing pH: at pH 8, depending on the water constituent, it corresponds to about half of the available ozone within 10 min (11). The $OH^{\cdot}$ radicals formed react very rapidly with many substances (for literature data see ref. 3), initiating known oxidations. The radicals are significantly more reactive than ozone and therefore less selective. Correspondingly, they are rapidly consumed by many of the available water constituents (S). Thus, the oxidation of specific impurities is strongly competed against by the presence of other constituents in the water (10, 11):


$\frac{1}{\eta'} \cdot O_{3,\Delta} \rightarrow OH^{\bullet}$
+ M
M_{oxide}
$\eta'' k'_M$
ΣS_i
$\emptyset$
k'_i

where: $O_{3,\Delta}$ is the quantity of ozone decomposed,

η' is the yield with which $OH^{\cdot}$ radicals were formed from decomposed ozone,

η'' is the yield with which OH˙ radicals, consumed by M, oxidize M,

k'_M, k'_i are the rate constants with which OH˙ radicals react with M or scavengers S_i,

and S_i are scavengers, including M, O_3, etc.

The elimination rate for this reaction is:

$$-\frac{d[M]}{dt} = \frac{dO_{3,\Delta}}{dt} \cdot \eta' \cdot \eta'' \cdot \frac{k_M'[M]}{\Sigma(k_i'S_i)}$$

2.1. Oxidation competition value of a water type (Ω_M)

For a batch or plug-type reactor the relative residual concentration of M at time t is:

$$\boxed{[M]_t/[M]_0 = e^{-O_{3,\Delta}/\Omega_M}} \qquad (3)$$

$$\Omega_M = \frac{1}{k'_M} \cdot \frac{1}{\eta' \cdot \eta''} \cdot \sum(k'_i\,[S_i]) \qquad (4)$$

On the basis of equation 3, the relative residual concentration of M plotted on a logarithmic scale against the quantity of decomposed ozone gives an elimination curve of slope $1/\Omega_M$ (see Fig. 3). Ω_M is a normalization value dependent on the water composition. It increases with increasing loading of the water with substances S_i that consume OH˙ radicals (see equation 4). If Ω_M does not essentially alter with ozonization, as happens in a large number of practical situations (cf. Section 2.4), and if M is an individual compound (not a sum parameter), the elimination curve is a straight line (see Fig. 3). In this case the residual concentration of M is 37% (= 1/e) of the initial value after the amount of the decomposed ozone has reached the value Ω.

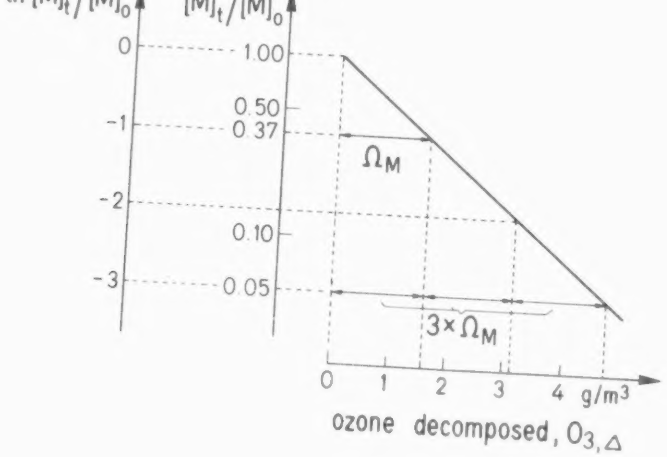


Fig. 3 Oxidation initiated by OH˙ radicals
Logarithmic fall of the relative concentration of an individual trace impurity M with increasing amount of ozone decomposed in water. Assumption: the Ω-value of the water is independent of ozonization

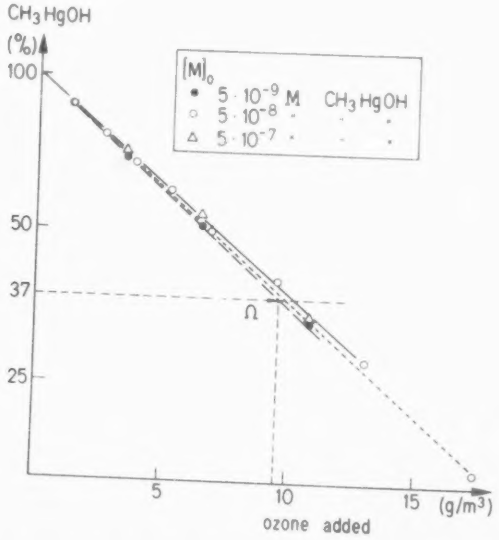


Fig. 4 Measured logarithmic fall of the relative concentration of methylmercury plotted against the amount of ozone added (mineralization of the methylmercury by OH˙ radical initiated reactions). Water loaded with 5 g/m^3 of octanol. pH 10.5; 0.05 M phosphate (9)

We suggest the following terms for the Ω-value:

German :	"Oxidationskonkurrier-Wert" (des Wassers)
English:	"Oxidation-competition value"
French :	"valeur de compétition à l'oxidation"

In principle, it is possible to calculate Ω_M for a specific compound M and a specific water composition according to equation 4 on the basis of relative rate constants well known for $OH^{\cdot}$ reactions (11). However, with such estimations some uncertainties regarding the yield factors η' and η'' always remain, and likewise regarding insufficiently characterized water constituents which are generally given only by sum parameters such as the DOC. It therefore seems better in practice to determine the Ω-value of a water experimentally with a suitable reference solute (12).

In the following it is shown on some examples that the concentration decreases found experimentally can be described by equation 3 and the Ω_M-value of equation 4.

Fig. 4 shows the measured oxidation of methylmercury to inorganic mercury(II) during ozonization (9). The water was "loaded" with a model substance (octanol). The observed oxidation of the methylmercury cannot be attributed to a "direct ozonization reaction" (9) (cf. Fig. 2), but the expected logarithmic decrease of the methylmercury concentration is obtained when the relative residual concentration is plotted against the quantity of ozone added (and decomposed) according to equation 3. As expected on the basis of equation 3, the course of the relative concentration lines does not change even when the initial concentration of the trace impurity is increased by some powers of 10. This means that the reaction is exactly of first order with respect to the trace impurity concentration. In addition, the slope of the relative concentration lines over the measured ozonization region remains constant. This means that Ω_M does not alter significantly with ozonization of the water. We obtained similar, but for analytical reasons somewhat more restricted, results for several other model substances, as well as for trace impurities detectable in lake water by gas chromatography (5, 8, 12).

The mineralization of methylmercury can be determined analytically particularly simply, exactly, and over a wide dynamic range. However, methylmercury forms complexes with many possible water constituents. Large complex-formation constants are already known for chloride, carbonate, phosphate, etc. However, since the reactivity of a compound is strongly affected by such complex formation (9), for characterizing a given water we recommend the use of inert reference solutes M, such as benzene or tetrachloroethylene.

Fig. 5 shows a Ω-value determination in a lake water that is (measured under Swiss conditions) strongly loaded. Here Ω only becomes constant after a "spontaneous ozone consumption" of about 0.5 g ozone/m^3. The "spontaneous ozone consumption" produces only a parallel displacement of the elimination lines. Even a preliminary ozonization with 10 g O_3/m^3 has only a limited influence on the residual slope of the elimination line (12).

(In waste water previously purified biologically the residual slope of the curves also changes only slightly with the degree of preliminary ozonization in the region of 0-10 g O_3/m^3 (10)). Constant Ω-values, i.e. constancy of the residual slopes of the logarithmic elimination lines, were observed in all the Swiss lake and ground water samples tested by us.

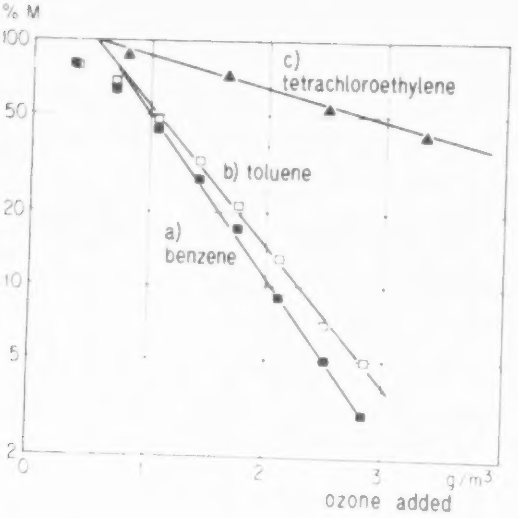


Fig. 5 Logarithmic decrease of the relative concentration of trace impurities plotted against the amount of ozone added. Water from Lac de Bret (DOC 4 g/m^3, Σ CO$_2$ ~ 1.6·M, pH ~ 8.3). Compounds added: a) 80 mg/m^3 benzene, b) 130 mg/m^3 toluene, c) 500 mg/m^3 tetrachloroethylene (12)

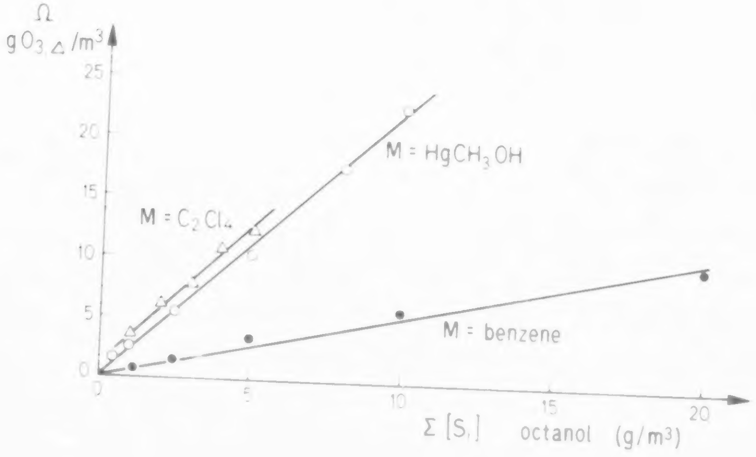


Fig. 6 Oxidation competition value Ω_M plotted against the DOC model loading (S = octanol). pH 10.5 (0.05 M phosphate). Compounds added: [Benzene]$_o$ = 80 mg/m^3, [HgCH$_3$OH]$_o$ = 10 mg/m^3, [C$_2$Cl$_4$] = 15 mg/m^3 (9)

The Ω-values of various water types are compared in Table 1, benzene and tetrachloroethylene being used as the reference solutes. In water of Lake Zürich the Ω-value for benzene at pH 8 was about 0.8 g of "ozone decomposed" ($O_{3,\Delta}$) per m^3 of water. This means that 0.8 g of decomposed ozone is sufficient to reduce the concentration of a compound such as benzene by a factor of e. An elimination to 5% of the initial concentration would necessitate $3 \times \Omega = 2.4$ g of "ozone-decomposed" per m^3 (cf. Fig. 3). At pH 10.5 the Ω-value rises to 4 g/m^3. For tetrachloroethylene, which reacts exceptionally slowly with $OH^{\cdot}$ radicals, the corresponding values are about 5 times as large (cf. also Section 2.3).

Oxidation effects of similar extents were measured in other drinking waters (11, 12).

Table 1 Examples of Ω-values for various water types

	pH	Ω ($g\ O_3/m^3$)	
		Benzene	Tetrachloroethylene
Lake Zürich b)	7,7	0,6	3,0
	10,5 a)	4,0	~26
Dubendorf c) ground water	7,6	1,0	6
	9,0 a)	3,0	~12

a) pH increased by addition of NaOH
b) Σ (CO_2) = 1.2 mM DOC = 1.2 mg/l
c) Σ (CO_2) = 2.6 mM DOC = 1.6 mg/l

2.2. The oxidation competition coefficient ω of various water constituents

Ω_M-values can be treated as composite magnitudes. The contribution of each constituent S_i can be calculated as the product of its concentration and a coefficient $\omega_{M,i}$:

$$\Omega = \frac{1}{\eta' \cdot \eta''} \cdot \frac{1}{k'_M} \cdot \Sigma\left(k'_i [S_i]\right) = \Sigma\left(\omega_i [S_i]\right)$$

or

$$\begin{aligned} \Omega = \omega_1 [S_1] + \omega_2 [S_2] + \quad & \omega_i [S_i] \\ + & \, \omega_j [S_j] \end{aligned} \qquad (5)$$

An experimental example of the calculation of the coefficients ω is given in Fig. 6, which shows the measured increase of Ω with increasing octanol content of a model water. We carried out similar measurements for water containing additions of bicarbonate ions, carbonate ions, free NH_3, and fulvic acids. The linear increase of the Ω-values observed with loading of a water corresponds formally to equation 5. The coefficients ω can be read off from the slope of the curves.

We propose the following terms for ω:

German :	"Oxidationskonkurrier-Koeffizient"
English:	"oxidation-competition coefficient"
French :	"coefficient de compétition à l'oxidation"

Table 2 gives some examples of measured coefficients ω. It can be seen that the $O_{3,\Delta}$ requirement that decreases the benzene value to 37% rises by 0.5 g/m^3 per g of octanol loading. The other values are given in mole/mole units. For bicarbonate the oxidation competition coefficient is about 1/10 as large as that for carbonate. That is, an elevation of the pH without elimination of carbonate leads to a strong increase of the ozone requirement. Even the effect of NH_3 (as an oxidation inhibitor) can be significant in the case of the oxidation of trace impurities in communal waste water pre-purified biologically if we work in the pH region in which ammonium ions are dissociated to free NH_3.

Table 2 Examples of coefficients ω for different water constituents (values from ref. 12)

S	pH	ω	
		Benzene	Tetrachloroethylene
Octanol	8-10	0,5 g/g	2,3 g/g
Fulvic materials a)	8-9	0,2 g/g	
$(HCO_3^- + CO_3^{2-})$	8,0	0,1 g/mole	0,6 g/mole
CO_3^{2-} b)	10,5	3,0 g/mole	13 g/mole
NH_4^+		0,0 g/mole	0,0 g/mole
NH_3	10,5	2,0 g/mole	10 g/mole

a) Soil fraction, soluble at pH 7 and at pH 1

b) Corrected for the proportion of bicarbonate

It is remarkable that the coefficients ω for NH_3 are higher than would have been expected on the basis of the low rate constants of the reaction of NH_3 with $OH^{\cdot}$ radicals (4). The reason is that the primary daughter products M_X formed from NH_3 very rapidly consume further oxidants, themselves becoming oxidized to nitrate. Only a part of the oxidation stages in this process is controlled by the oxygen molecules present; experience shows that the consumption of ozone for the oxidation of NH_3 to nitrate is really large ($\eta' \cdot \eta'' < 0.25$).

2.3. Ratios of the Ω_M-values for different trace impurities (M) in a water

As can be seen from equation 4, the Ω_M-values of a given water for different reference solutes M vary in inverse proportion to the rate constants, and a correction is still needed for different yield factors η''. For the ratio of the Ω-value of a reference solute A to that of reference solute B, equation 4 gives:

$$\Omega_A/\Omega_B \propto k'_B/k'_A \times (\eta''_B/\eta''_A) \qquad (6)$$

For the oxidations that are only initiated by secondarily formed oxidants only the reaction of the $OH^{\cdot}$ radicals is significant in the systems investigated here by us. Therefore, in equation 6 only the relative reaction rate of the $OH^{\cdot}$ radicals need be considered. Our earlier measurements on other model solutions led to a similar result (3). The special findings that in the systems tested here the hydroperoxide radicals ($HO_2^{\cdot}$ or O_2^{-}) do not initiate oxidation of the reference solutes was specially checked, the $OH^{\cdot}$ radicals being converted into $HO_2^{\cdot}$ radicals by the addition of H_2O_2: in the case of benzene and tetrachloroethylene the H_2O_2 additions caused a positive contribution to the Ω value, which was, however, not yet constant.

Fig. 7 shows the ratios expected on the basis of the constants cited in the literature. The rate constants k_M, with which the $OH^{\cdot}$ radicals react with the corresponding trace impurity M are given on the left ordinate (see ref. 3 for literature). The scale on the right gives a reference point for the expected Ω_M-values. This scale is calculated with the aid of equations 3 and 4 and is normalized for the case in which the water has a $\Omega_{benzene}$-value of 1 g/m^3 (the waters of Lake Zürich, Lake Constance, ground water in Zürich,etc. have somewhat lower normalization values ($\Omega \sim 0.8$ g $O_{3,\Delta}/m^3$)). In addition, it is assumed that the yield factor η" is in all cases the same as for benzene. This assumption is justified on the basis of our present experience, provided that only an estimation of the ratios is required. From Fig. 7 it is not sufficiently clear that for the usual organic compounds k' values of comparable magnitude are obtained, since substances that display an exceptionally low reactivity were used on purpose.

Consultation of more detailed tabulated values shows, however, that the rate constants k' of the majority of organic compounds of average molecular weight are situated in a region that extends from tetrachloroethylene to a little above benzene.

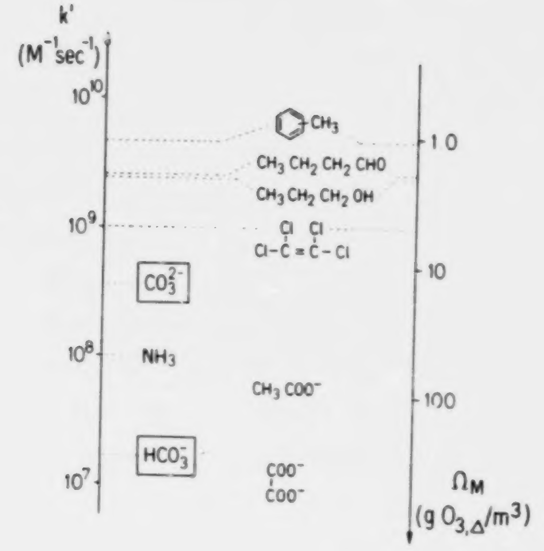


Fig. 7. Left-hand scale: Examples of rate constants with which OH· radicals react with trace impurities (for literature see ref. 3). Note that substances with $k < 10\ M^{-1}\ sec^{-1}$ are taken to be special exceptions
Right-hand scale: Oxidation competition value Ω_M. Scale normalized to $\Omega_{benzene} = 1.0$ (average value found for Swiss lake water, pH ~ 8). It is assumed that $\eta''_M \equiv \eta''_{benzene}$

It follows from Fig. 7 that in a type of drinking water expected for Swiss conditions (provided pH < 8.5) at a decomposition of 1-10 g of ozone per m^3 a reduction of many of the possible trace impurities by a factor of "e" can be reckoned with. A reduction to 5% would require about 3 times this Ω-value of ozone (cf. Fig. 3).

Measurements of the behaviour of the organic trace impurities present in the water of Lake Zürich in concentrations of only $\mu g/m^3$, such as toluene, xylene, chlorobenzene, etc. show that these eliminations too correspond quantitatively to the principles outlined here (5,6).

2.4. Phenomenon of constant Ω-values

In principle the Ω_M-value is given by the slope of the products' elimination graphs plotted on a logarithmic scale according to equation 3. These curves are mostly represented by a straight line for reference solutes in natural water and even in waste water that has previously been biologically purified. In some waters a correction must however be made for an initial spontaneous ozone consumption manifested by a straight line not passing through zero. However, the residual slope even in these cases depends only slightly on the preliminary ozonization, so long as this occurs with only a small quantity of ozone which is usual in the treatment of drinking water. The phenomenon that Ω is almost independent of ozonization (the slope of the elimination curve is constant) simplifies many estimations, but should not be regarded as a matter of course. The fact that Ω-values frequently remain constant after a small spontaneous ozone consumption can be explained as follows:

a) An essential proportion of the Ω-value is based on the contribution of bicarbonate and of the content of carbonate ions in the water (11). If the pH of the water does not change, this contribution hardly changes during the ozonization.

b) Another essential proportion of the Ω-value is based on the $OH^{\cdot}$-consuming action of "humic substances" and other refractory organic compounds, mostly of higher molecular weight. Oxidation of these scavengers changes the degree of oxidation and perhaps also the molecular weight of these compounds. However, the reactivity of the whole organic material with respect to the OH˙ radicals is scarcely affected by this. Even water in which a DOC loading is simulated only by the addition of octanol displays a Ω value independent of ozonization. In this case the constancy of Ω is based on the use of a DOC model compound in which the sum of the oxidation products formed and the starting substance consume the OH˙radicals at similar rates (for a detailed discussion see ref. 12).

c) Even the effect of a substance such as NH_3 changes only slowly with advancing ozonization: the free NH_3 reacts really sluggishly (4), and, if the pH is considerably less than 9, the water contains a large reservoir of unreactive ammonium ions from which NH_3 can always be released in accordance with the equilibrium conditions.

Many other water constituents, however, lose their radical scavenger effect as the ozonization progresses. In water in which such constituents become decisive the Ω-value changes in accordance with the ozonization. Such substances seem to have only a subordinate significance in our drinking waters.

In principle, OH˙ radicals can also be consumed by ozone molecules themselves (12), in which case the Ω-value would be expected to change with the nature of the ozone input. The proportion of ozone in the over-all Ω decreases with increasing instantaneous ozone concentration and increasing cleanliness of the water. However, an experimental determination of the ω_{O_3} coefficient may prove really difficult.

The substance to be measured M also gives a contribution $\omega_M[M]$ to the Ω value. If the sum of the oxidation products formed from M gives a contribution different from the starting substance, the over-all Ω-value of the water will change with progressing ozonization. This only decreases in weight if M is not a true trace but a strong impurity. In such cases the ozonization effect is more simply described on the basis of the ozone yield $(\Delta M/O_{3,\Delta})_o$, as is obtained for low conversions (start of the ozonization). The kinetics of such systems have been treated in earlier papers (9). The characterization of an ozonization system with the aid of the Ω values as suggested in the present work is, however, generally more informative and always suitable when the water properties with respect to indirect oxidation effects of the ozonization are to be characterized.

In the cases investigated the same coefficients ω were found in model phosphate buffer solutions as in lake water or ground water. When using a borate buffer (0.05 M) however, we observed an increase of all ω-values, which at the moment we can only explain by an alteration of the η' value caused by the borate.

3. Cooperation of the direct reaction of ozone and the radical mechanism

Since ozone has a very high substrate selectivity, very few substances are included by chance in a region in which they are simultaneously oxidized essentially by the ozone and by the ozone-decomposition products. In the treatment of drinking water with a pH of about 8, i.e. a water in which half of the ozone decomposes within about 10 min, this may be just the case for xylene (cf. Fig. 2). For a compound such as benzene the "direct O_2 reaction" already plays a part about 100 times smaller. On the other hand, phenol-like trace impurities are degraded 100 times faster directly by ozone than the ozone can decompose at pH 8.

There is an important difference between the two types of reaction: the two types of oxidation lead to different intermediate products, i.e. different daughter products, which can become concentrated in the water, and they are governed by different ozonization process parameters. The "direct O_3 reaction" can be improved by increasing the ozone stability. The indirect reaction, however, the "$OH^{\bullet}$ radical reaction", is based on a decomposition of ozone, and in contrast to the "direct O_3 reaction" it is inhibited by constituents such as bicarbonate or carbonate. This property of the $OH^{\bullet}$ radical reaction allows the extent of the reaction to be ascertained experimentally, by determining the effect of the addition of relatively inert substances such as bicarbonate (5, 11) or butanol, octanol, etc.

(1) GILBERT, E.
Chemische Umsetzungen und Reaktionsprodukte bei der
Ozonbehandlung von Trinkwässern
(see paper Gilbert, this publication)

(2) TAUBE, H., BRAY, C.
Chain Reactions in Aqueous Solutions Containing Ozone,
Hydrogen Peroxide and Acid
J. Am. Chem. Soc. 62 (1940), 3357-73

(3) HOIGNE J., BADER, H.
The Role of Hydroxyl Radical Reactions
in Ozonation Processes in Aqueous Solutions"
Water Res. 10 (1976), 377-386

(4) HOIGNE, J., BADER, H.
Ozonation of Water: Kinetics of Oxidation of Ammonia
by Ozone and Hydroxyl Radicals
Environm. Sci. & Techn. 12 (1978), 79-84

(5) HOIGNE, J., BADER, H.
Kinetik und Selektivität der Ozonung organischer Stoffe
in Trinkwasser
Wasser Berlin 77, Tagung der Fachgruppe Wasserchemie
in der GDCh (Colloquium Verlag Berlin 1978), 261-276

(6) HOIGNE, J., BADER, H.
Rate Constants for Reactions of Ozone with Organic Solutes in Water
To be published

(7) SCHALEKAMP, M.
Die Erfahrungen mit Ozon in der Schweiz, speziell hinsichtlich der Veränderung von hygienisch bedenklichen Inhaltsstoffen
Wasser Berlin 77, Tagung der Fachgruppe Wasserchemie in der GDCh (Colloquium Verlag Berlin 1978), 31-69

(8) ZÜRCHER, F., BADER, H., HOIGNE, J.
To be published

(9) HOIGNE, J., BADER, H.
Ozone and Hydroxyl Radical Initiated Oxidations of Organic and Organometallic Trace Impurities in Water
175th Am. Chem. Soc. Meeting, Anaheim 1978, ACS Symp. Series (in press)

(10) HOIGNE, J., BADER, H.
Ozone Initiated Oxidations of Solutes in Wastewater: A Reaction Kinetic Approach
Progr. Water Technol. 10 (1978), 657-671

(11) HOIGNE, J., BADER, H.
Beeinflussung der Oxidationswirkung von Ozon und OH$^{\cdot}$-Radikalen durch Carbonat
Vom Wasser 48 (1977), 283-304

(12) HOIGNE, J., BADER, H.
To be published

TRANSFORMATION OF HUMIC ACIDS BY OZONE

J. Mallevialle

It is no longer necessary to stress the advantage of following the course of humic-type natural organic materials through the different stages of water treatment with a particular mention of the use of oxidizing agents. The action of chlorine on the humic and fulvic acids of water, in particular with the formation of halomethanes, has been described in many publications (1, 2). In our laboratory we are working on the action of ozone, which is often described as being very effective in decolorizing natural water, but we are not confining ourselves to strongly coloured water, since we believe that a large part of the organic material in water can be compared to humic and fulvic acids - referred to as "HA" hereafter (3).

1. THE DECOMPLEXING ACTION OF OZONE

The structure scheme proposed by Gjessing (Fig. 1) (4) illustrates one of the first consequences of the ozonization of humic acids. These acids have a "core" at the periphery of which mineral elements may be found in addition to organic compounds such as pesticides (Lindane or D.D.T.). When ozonization takes place, these various elements are released into the water;the iron precipitates in the form of ferric hydroxide, the manganese may be converted into MnO_4^- ions giving a violet tinge to the water, and the organic compounds little attacked by ozone may be found in the water, as happens for example in the case of Lindane. We have already described this type of phenomenon in previous publications (5,6).

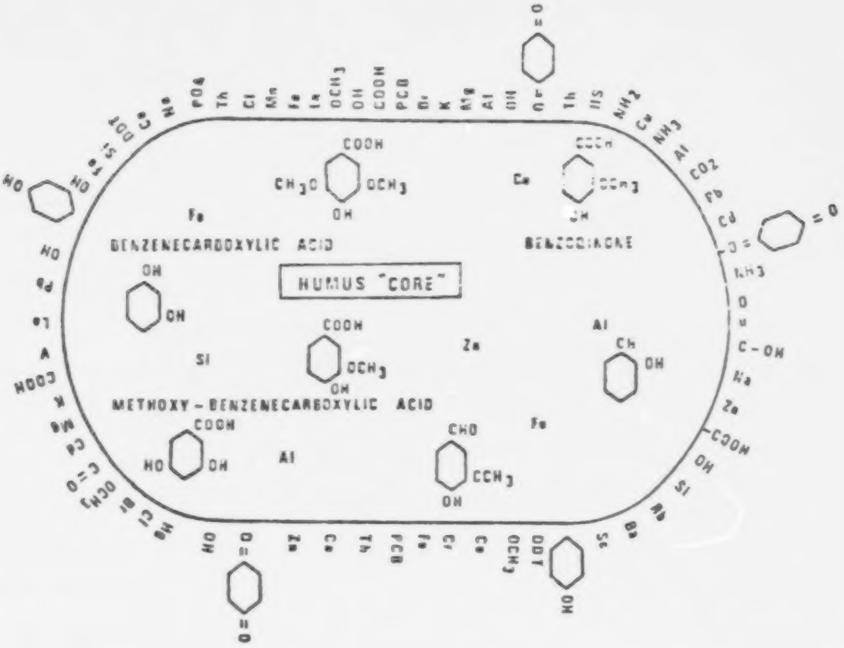


Fig. 1 Schematic structure of humic acids (after Gjessing)

2. STUDY OF THE OZONIZATION BY-PRODUCTS

2.1. Compound-identification tests

If one considers the example of the humic acid core structure put forward by Schnitzer and Khan (Fig. 2) (7), two important observations may be made:

a) During the ozonization of natural organic substances a large quantity of by-products is formed, the number and nature of which will depend on the type of the water and the amount of ozone used. Detailed analysis of these by-products is complicated because of their diversity and the difficulty of obtaining reference compounds. With small quantities of ozone we observe depolymerization with liberation of phenolic or quinonic "monomers"; this is what we observed, for example,

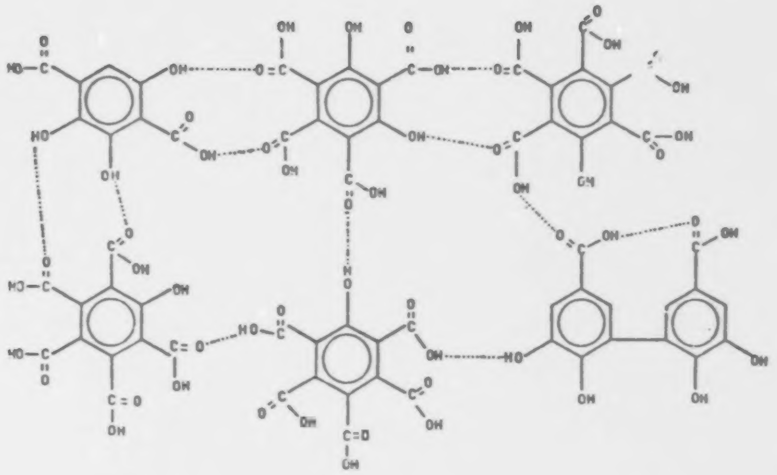


Fig. 2 Suggested structure of the humic acid "core" (after Khan and Schnitzer)

by thin-layer chromatography. With larger quantities of ozone we observed the opening of benzene rings and the formation of aliphatic aldehydes and acids, as has been shown by many authors working on the ozonization of phenols (8,9).

b) Humic acids are not well-defined compounds but complex mixtures of organic compounds in constant evolution, for which it would be difficult to determine characteristics other than by over-all techniques.

2.2. Search for parameters permitting the transformation of the HA by ozone to be studied

Curves 3 and 4 represent the variation of various parameters in the course of ozonization of a strongly coloured water free of any industrial pollution (little-mineralized water containing 20-40 mg/l of dissolved organic carbon) (10). We preferred to select a real case rather than a solution of HA extracted from a given soil. Fig. 3 is an example of the results we obtained, confirming the comments in the preceding

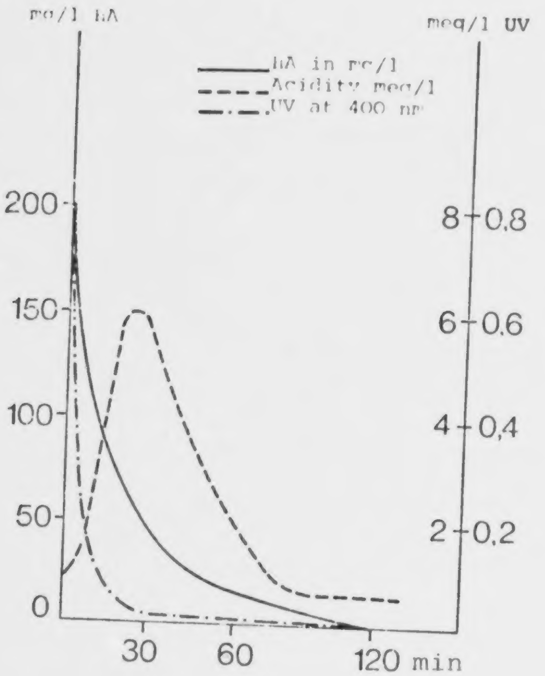


Fig. 3

Elimination of humic acids as a function of ozonization time

section. The colour disappears very rapidly, while the concentration of COOH groups goes through a maximum and diminishes more or less rapidly. The HA content, measured by the reduction of phosphotungstic and phosphomolybdic acids (polyhydroxy aromatics dosage (11)) decreases much more slowly than the colour.

2.2.1. Over-all parameters of the type of the TOC, COD, TOD, and BOD_5

Fig. 4 shows the variation of several over-all parameters currently used in this field as a function of the time of ozonization. Here again it is found that the colour disappears very rapidly. The COD and TOD follow approximately the same course. For low amounts of ozone we observed an increase in the BOD_5, which goes through a maximum before falling off markedly. The conclusion from this type of results is that we have transformed the organic materials present into more bio-degradable compounds containing more and more oxygen without reaching total oxidation.

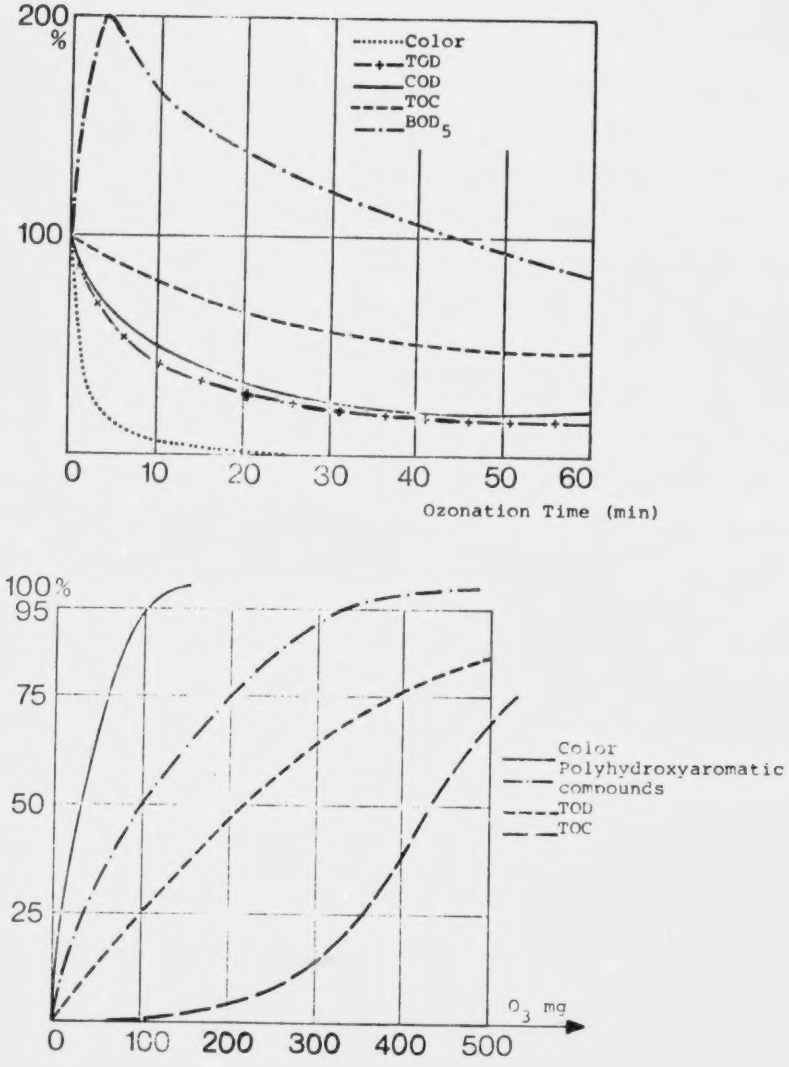


Fig. 4 Ozonization of natural waters

2.2.2. Other parameters

Since the determinations of BOD_5 and TOD are difficult in the case of low concentrations, we felt it important to look for other characteristic parameters sufficiently sensitive to be applied in the sector of the production of drinking water. We have thus been led to use the absorption at 254 nm currently applied in certain countries (12), and in particular the fluorescence intensity in ultra-violet light.

The latter in fact provides two elements of characterization (Fig. 5), the fluorescence intensity, which is proportional to the concentration, and the maximum emission wavelength λ_{em} which, on the basis of our experience, is determined by the degree of polymerization or size of the molecule. The larger is the molecule, the more is λ_{em} displaced towards longer wavelengths. For example, Seine water upstream of Paris has a λ_{em} of 415 nm, while downstream of Paris its λ_{em} is only 405 nm (13).

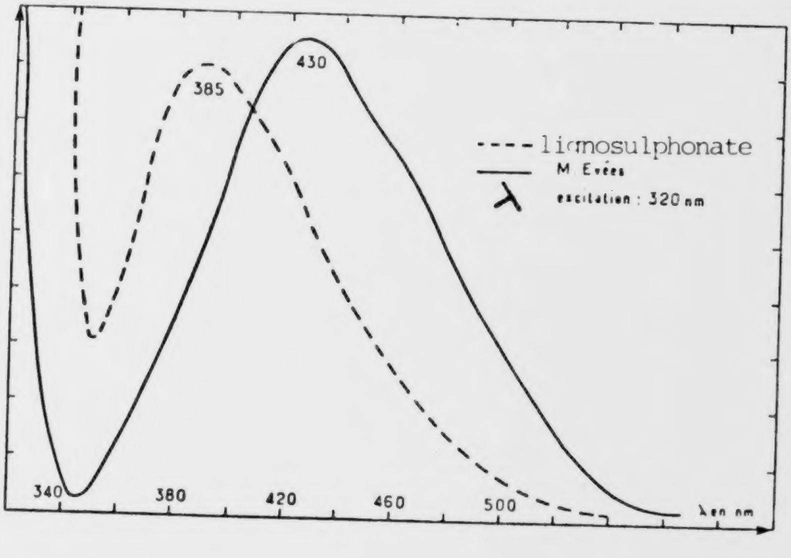


Fig. 5 Fluorescence spectra of a solution of lignosulphonates and of a solution of humic materials

While working on a contract for the Ministry of the Environment we established significant correlations between the fluorescence intensity and the various over-all parameters described in Section 2.2.1. These correlations were based on 500 water samples divided into different types according to their nature or origin. By way of example, Table 1 shows the values obtained for the pair of parameters "fluorescence" and "organic carbon". The correlations are significant in all cases where it is not desired to carry out an oxidation treatment by ozone. This result can be easily understood if one considers the results in Fig. 6, showing the variation of these parameters as a function of the time of ozonization.

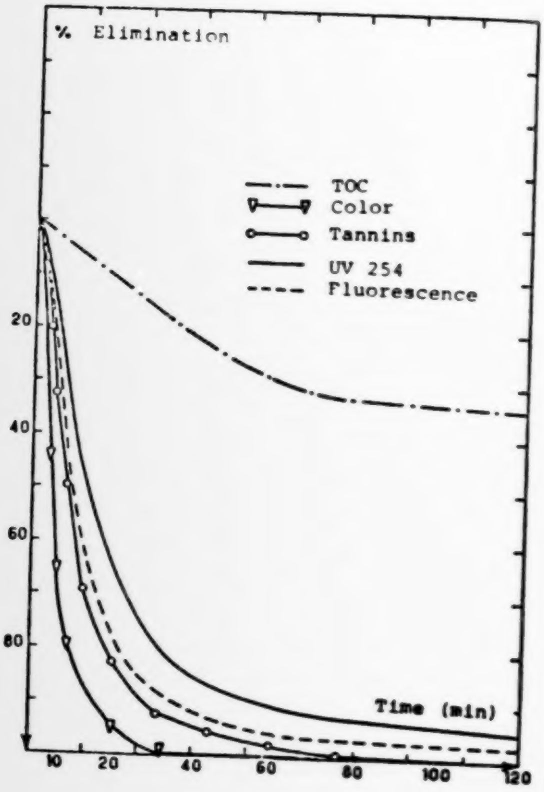


Fig. 6

Ozonization of natural waters

TABLE 1 Tests of the correlation fluorescence = f (TOC) for various waters

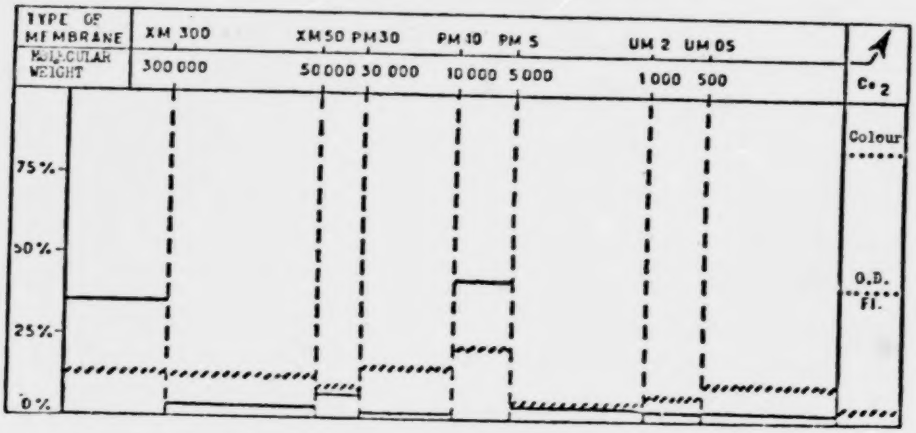
	All Classes	Raw Water	Decanted Water	Filtered Water	Ozonization	Chlorination
Correlation Coefficient	0,867	0,911	0,502	0,528	0,177	0,973
Equation	(F)=0,670(C) + 1,038	(F)=0,676(C) + 1,415	(F)=0,995(C) + 0,268	(F)=0,684(C) + 0,686	(F)=-0,136(C) + 0,10	(F)=0,626(C) + 1,654
No. of Degrees of Freedom	515	212	83	211	27	68
Significance Level	<0,1%	<0,1%	<0,1%	<0,1%	> 10% < 25%	<0,1%

	Morsang	Viry	Suresnes	Croissy	Aubergenville	Mare aux Evées	Various
Correlation Coefficient	0,713	0,363	0,000	0,200	0,225	0,543	0,417
Equation	(F)=0,746(C) + 0,37	(F)=0,502(C) + 1,06	(F)=-0,01(C) + 3,96	(F)=0,12(C) + 3,46	(F)=0,248(C) + 3,3	(F)=0,267(C) + 19,2	(F)=0,637(C) + 0,868
No. of Degrees of Freedom	132	84	50	66	87	18	61
Significance Level	<0,1%	<0,1%	not significant	> 5% <10%	> 1% <2,5%	>0,1% < 1 %	<0,1%

Thus, we have just seen that the over-all parameters used by us vary in a noticeably different manner in the course of an oxidation treatment. While the TOC gives the absolute value of the number of atoms of dissolved organic carbon, it gives no indication of the chemical nature of the organic compounds present. On the other hand, fluorescence, for example, indicates the presence of cyclic compounds without giving their content in absolute value, since we have here a mixture of compounds. The parameters we have described are thus in fact complementary, and we believe it is essential not to calculate the elimination yields of the organic materials in relation to just one of these parameters, in view of the risk of grave errors.

2.2.3. Techniques of separation on membranes

As has been demonstrated by certain authors (4), natural waters containing HA are complicated solutions of organic compounds with widely different molecular weights. The technique of ultrafiltration through Diaflo-Amicon membranes makes it possible to fractionate the organic compounds according to different ranges of molecular weight. Here again we believe that it is necessary to use several parameters for characterizing the organic material. (We have retained the TOC, absorption at 254 nm, and fluorescence). The ultrafiltration technique has also enabled us to verify that the HA emission maxima are a function of their degree of polymerization. Fig. 7 shows an example of this type of separation with a water described in Section 2.2. After ozonization that eliminated 80% of the colour, 30% of the fluorescence and of the 254-nm absorption, and finally a certain percentage of the organic carbon, we find an increased homogeneity of the distribution, explained by transformation of the HA into compounds of lower molecular weight.



Fractionation of HA into different ranges of molecular weight

——— TOC before ozonization ⁓⁓⁓ TOC after ozonization

Fig. 7

3. VARIATION OF THE OVER-ALL PARAMETERS FOR SOME APPLICATIONS OF OZONE

3.1. Effect of preliminary ozonization on the effectiveness of coagulation

We ran laboratory tests on the effect of preliminary ozonization with small amounts of ozone (0.1 - 2 mg/l) on about 30 samples of Seine water (TOC of the order of 4 mg/l) and some samples of lake water containing humic acids (TOC about 10 mg/l). In the great majority of cases after ozonization we observed an increase in turbidity and a reduction of the absorption at 254 nm and of fluorescence, proportional to the amount of ozone used, while the variations in the TOC were of the order of 0.1-0.2 mg/l (see, for example, **Table 2**). These ozonizations were effected by passing 30 litres of water through a 5-litre reactor. We then ran comparative jar tests on the water with and without ozonization. In the majority of cases for a given amount of coagulant, differences of 5-30% were observed in favour of pre-ozonization in the elimination of the absorption at 254 nm and fluorescence. In contrast, this improvement was only of the order of 0.1-0.2 mg/l in the case of organic carbon (raw water 3-4 mg/l). It is probable that in a pilot or industrial installation the elimination of organic carbon would be greater due to biological degradation in the sand filter; at least this is what we are trying to demonstrate at the moment on a pilot installation (2 m^3/h).

TABLE 2 Effect of pre-ozonization (1 mg O_3/l) on the efficacy of coagulation of Seine water by aluminium sulphate with coagulant aid

NON-OZONIZED RAW WATER

AMOUNT OF COAGULANT (mg/l)	0	20	40	60	80	100
Flocculation eval. (15 min)	0	2	5	5	3	3
Turbidity (drops of mastic)	48	25	16	18	23	23
Optical density at 254 nm (referred to 1 m)	7,52	5,02	3,72	3,28	2,76	2,46
Fluorescence (mV)	0,64	0,62	0,57	0,54	0,49	0,47
Total organic carbon (mg/l)	3,3	2,9	2,3	2,2	1,9	1,6

OZONIZED RAW WATER (1 mg/l of O_3)

AMOUNT OF COAGULANT (mg/l)	0	20	40	60	80	100
Flocculation eval. (15 min)	0	2	3	5	4	3
Turbidity (drops of mastic)	51	25	23	20	25	29
Optical density at 254 nm (referred to 1 m)	5,98	3,42	2,88	2,32	1,96	1,86
Fluorescence (mV)	0,42	0,37	0,32	0,23	0,23	0,28
Total organic carbon (mg/l)	3,3	2,7	2,1	2,[illegible]	2,2	1,3

We have also tried to explain the increase in turbidity observed after ozonization by counting the particles in a Coulter counter (Figs. 8 and 9).

In most cases we observed an increase in the total particle count, with a slight reduction in the number of large particles, as shown in Fig. 9.

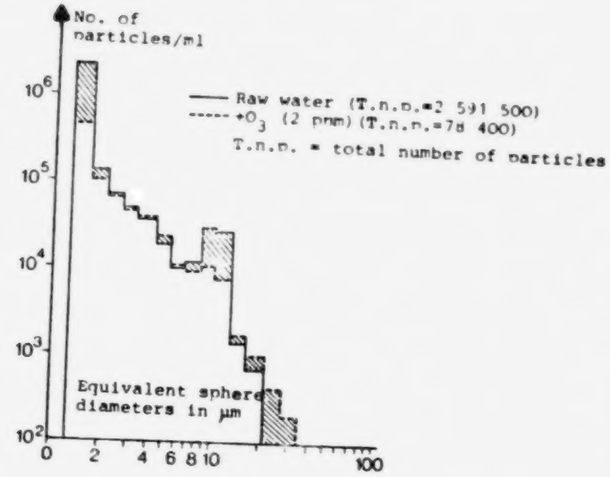


Fig. 8

Cholet water

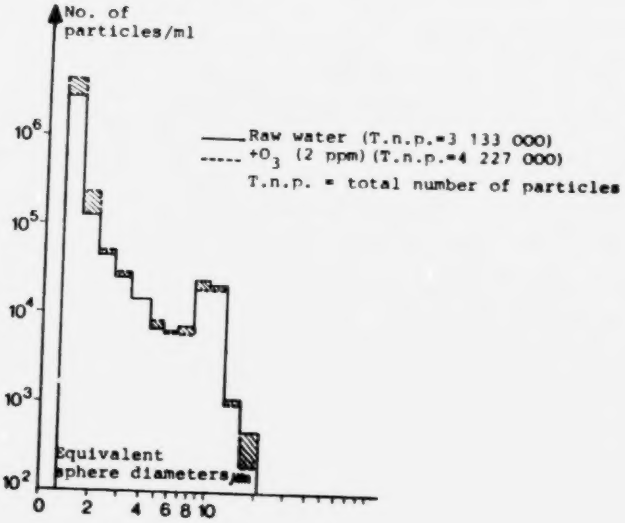


Fig. 9

Cholet water

3.2. Effect of ozonization on filtration on granular carbon

Fig. 10 shows the flow diagram of a waterworks for treating Seine water upstream of Paris. Three industrial lines and a pilot line provide a comparison of the efficacy of different combinations of ozonization and filtration in a refining treatment. We shall not list here the results on the elimination of micropollutants, since this has already been done and will be dealt with in various publications (14). We have simply indicated by way of example the variation in the fluorescence/organic carbon (=F/C) ratio. It is noted that after each ozonization operation F/C diminishes markedly and increases again after filtration through granular carbon, which confirms the results we obtained in the first part of this study.

3.3. Biological degradation of organic materials

Fig. 11 is a flow diagram of a waterworks for the treatment of Seine water downstream of Paris. The two parallel industrial lines (continuous lines) are based on two different principles, one (Chabal type) using slow filtration, the other using standard clarification treatment with the addition of powdered active carbon. Over several months of operation these two lines give equivalent results on the basis of the organic carbon as a parameter. On the other hand, the absorption at 254 nm and in particular the fluorescence are much greater at the outlet of the slow filtration line.

Furthermore, the maximum emission wavelength of fluorescence is greater in this last line. Two explanations are possible: the slow filtration has a smaller eliminating effect on humic acids of high molecular weight, or the phenomenon is caused by the formation of metabolites of relatively high molecular weight by microorganisms. This is what we intend to study during the coming months.

Fig. 11 also shows, by means of the broken lines, an experimental line in which preliminary oxonization is carried out before the slow filtration stage. The results obtained should enable us to confirm the increased bio-degradability of organic materials after oxidation with ozone.

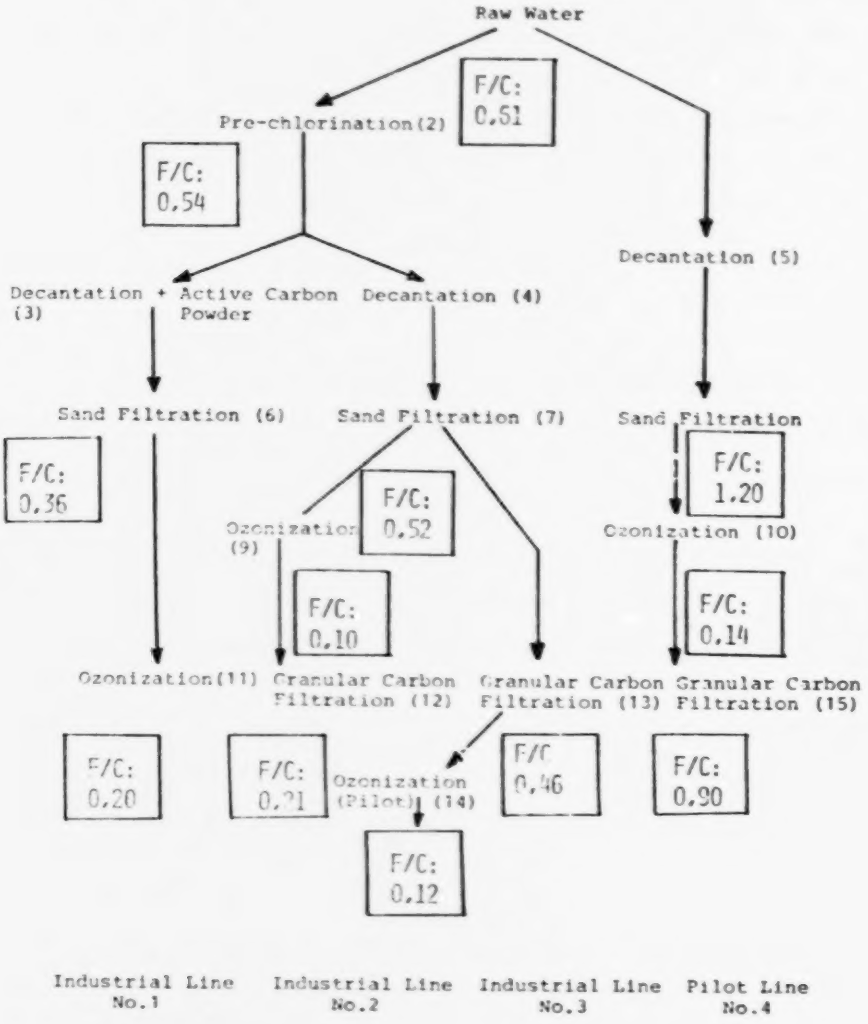


Fig. 10 Morsang/Seine Waterworks
Flow diagram of different lines of treatment

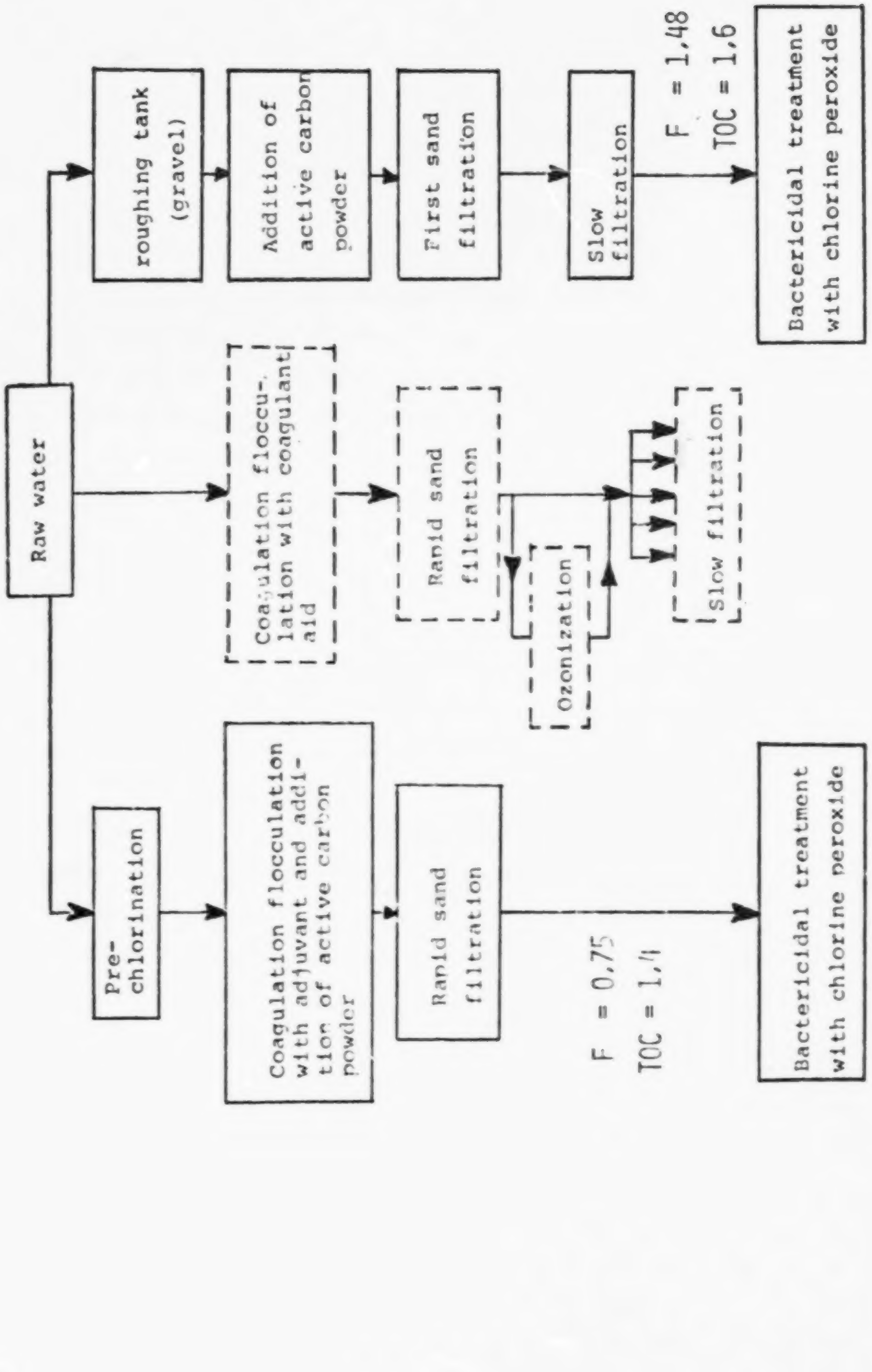

Raw water
Pre-chlorination
Coagulation flocculation with adjuvant and addition of active carbon powder
Rapid sand filtration
F = 0,75
TOC = 1,4
Bactericidal treatment with chlorine peroxide
Coagulation flocculation with coagulant aid
Rapid sand filtration
Ozonization
Slow filtration
roughing tank (gravel)
Addition of active carbon powder
First sand filtration
Slow filtration
F = 1,48
TOC = 1,6
Bactericidal treatment with chlorine peroxide

Fig. 11

4. CONCLUSION

Several observations may be made about the various tests carried out:

- It is practically impossible to achieve total degradation of natural humic-type organic materials by means of ozone. In the majority of cases there is a conversion of these organic materials into compounds of lower molecular weight. A practical conclusion may thus be drawn: The time of contact and the amount of ozone must not be reduced more than it is necessary, and it will often be advisable to follow the ozonization with a filtration treatment, e.g. on granular active carbon.

- When the different behaviour of various waters with respect to oxidizing agents such as ozone is considered, it must be realized that each water constitutes a special case and that a study of the ozonization by-products will be very difficult in view of their extreme diversity.

- When carrying out oxidation treatments it seems important to us to have available a selection of parameters of the type described. Elimination yields calculated just on a single parameter will in most cases lead to wrong conclusions.

(1) ROOK, J.J.
Formation of haloforms during chlorination of natural waters
Water Treatm. Examin. 23 (1974), 234

(2) STEVENS, A.A., SEEGLER, D.R., SLOCUM, C.J.
Products of chlorine dioxide. Treatment of organic materials in water
I.O.I. Workshop Ozone/Chlorine Dioxide Oxidation Products of Organic Materials. 17-19 Nov. 1976, Cincinnati, USA

(3) SONTHEIMER, H.
Conference at Karlsruhe, Federal Republic of Germany (1975)

(4) GJESSING, E.T.
Physical and chemical characteristics of Aquatic Humus
Ann Arbor Sciences (1976)

(5) BUFFLE, J.Ph., MALLEVIALLE, J.
Le rôle des matières humiques envisagées comme agent d'accumulation et véhicule des substances toxiques dans les eaux
Techniques et Sciences Municipales, n°spécial juin(1974), 331-340

(6) MALLEVIALLE, J.
Degradation of humic substance in water by different oxidation agents (ozone, chlorine, chlorine dioxide)
I.O.I. Workshop Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, 17-19 Nov. 1976, Cincinnati, USA

(7) SCHNITZER, M., KHAN, S.U.
Humic substances in the environment
Marcel Dekker, New York (1972)

(8) EISENHAVER, H.R.
The ozonation of phenolic wastes
J. WCPCF 40 (1968), 1887

(9) DORE, M.
Ozonation des phénols et des acides phénoxy-acétiques
Water Research 12 (1978), 6,

(10) MALLEVIALLE, J.
Les agents complexants naturels des eaux
Etude des propriétés physico-chimiques des matières humiques et de leur transformation par ozonation
Thèse présentée à l'Université Paul Sabatier de Toulouse (Nov. 1974)

(11) -
Standard Methods for the Examination of Water and Waste Water
13 Ed., 346

(12) SONTHEIMER, H. et al.
The Mülheim Process
J. AWWA 70 (1978), 7, 393-396

(13) MALLEVIALLE, J.
Etude de la signification de la fluorescence dans les eaux dans ses rapports avec leurs qualités exécutée pour le Ministère de l'Environnement (Avril 1978)

(14) RICHARD, Y., FIESSINGER, F.
Emploi complémentaire des traitements ozone et charbon actif
3ème Congrès International de l'Institut International de l'Ozone, 4-6 Mai 1977, Paris

OZONE AND HALOGENATED ORGANIC COMPOUNDS

E. de Greef, J. Hrubec and J.C. Morris

1. Introduction

Advances in the analytical determination of organic compounds in water and the discovery of the formation of halomethanes during chlorination are the most important factors leading to the initiation of a number of studies on the influence of ozonation on halogenated substances in drinking water. During the initial period, after the finding of the formation of trihalomethanes, special attention was paid to the effects of ozone, which was proposed as one of the most hopeful alternative oxidants to chlorine, and to the removal of halomethane precursors, as well as to the removal of halomethanes themselves. During a more recent period interest has been focused more upon the general influence of ozonation on the presence of halogenated compounds.

In the following paper the influence of ozonation on the occurrence of halogenated organic compounds is discussed. Special attention is paid to the combination of ozonation with breakpoint chlorination in relation to observed changes in the concentrations of halomethanes. In addition to this, possible mechanisms for observed phenomena are proposed.

2. Formation of Halomethanes by Chlorination Following Pre-ozonation

The influence of preoxidation by ozone on the formation of halomethanes has been studied intensively by Rook (1,2) and Montiel (3). These studies have been carried out under conditions similar to those in practice with regard to the dose of ozone, pH and temperature of the treated water.

The use of preozonation to reduce the formation of halomethanes was based on the assumption that ozone, being the stronger oxidant, would destroy or oxidize those sites in the organic molecule which are suited for the formation of halomethanes (2).

From Table 1 it can be seen that pre-ozonation as a part of the water treatment at two Rotterdam Water-Works and the Paris Municipal Water-Works at Orly has no substantial effect on the reduction of halomethanes when the water is subsequently chlorinated.

Also, according to the results of studies by the E.P.A. (6) ozone at a dosage level less than 5 mg/l will not decrease the concentration of trihalomethane precursors.

The described findings are only valid for the application of pre-ozonation without subsequent adsorption on activated carbon and without additional biological processes like slow sand-filtration (7). Also the combination of ozonation with ultra-violet radiation does not apply because in these combinations the application of U.V. seems to provide a positive contribution to the increased removal of both organic matter together with halomethane precursors (6,9).

TABLE 1 Formation of halomethanes (μg/l) by use of ozone prior to chlorination (lit. 2,3)

Contact time after ozonation (in hours)	Water treatment plant:						
	Orly	Rotterdam-Kralingen			Rotterdam-Berenplaat		
	$CHCl_3$	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$
0.15	20	22	8	8	4	2.3	2.5
4 - 5	30	27	11	9	7	2.5	2
24	50	30	11	7	12	5.5	3
without ozone	-	32	18	11	12.5	5.8	2.5

Furthermore, it should be noted that also some laboratory studies have indicated that, when the ozonation is used prior to chlorination, the ozone did remove precursors and consequently reduce the halomethane content to some extent (4,5,6).

It seems that only additional studies directed to improving our knowledge of the chemistry of ozonation reactions with organic substances, particularly the mechanisms and kinetics involved, can provide a better insight into the problem of preozonation and halomethane formation.

3. Removal of Halomethanes by Ozonation

The tests which have been carried out to study the effects of ozonation on the removal of halomethanes (3,4) have shown that ozone, under the conditions of water treatment practice and at the level of ozone doses concerned, does not decrease the concentrations of halomethanes already formed prior to ozonation. Only with unrealisticially high doses of ozone does removal of halomethanes seem to occur and even then the removal may be a result of volatilization (9).

4. Influence of Ozonation on the Behaviour and Formation of Halogenated Organic Compounds

The most extensive data with regard to the influence of ozonation on halogenated organic compounds have been published by Stieglitz et al. (10). These data are based on the measurement of chlorinated organic compounds at several German water treatment plants which use ozone and are situated along the river Rhine. Results on the occurrence of halogenated organic compounds were obtained by means of determinations of dissolved organic chlorine (DOCl), non-polar dissolved organic chlorine (DOClN) and gaschromatographically detectable organic chlorine (GOCl), and further by means of identification of different halogenated compounds by GC-MS. As can be seen, Table 2 shows a substantial increase in DOCl-N as well as the gaschromatographable organic chlorine after ozonation of a bankfiltered water. Furthermore, like chloroform, tetrachloromethane, trichloroethylene, tetrachloroethylene, tetra- and hexachlorobutadiene have increased in measured concentrations as a result of ozonation.

TABLE 2 Organic chlorine within different treatment steps for a Rhine water utility using ozonation (8)

	Chlorine µg/1		
Sample	Dissolved Organic Chlorine	Dissolved Organic Chlorine Nonpolar	Gaschromatographically Detectable Organic Chlorine
Rhine water	99	15	9.5
Sandbank Filtrate	61	4	4.8
Ozonated Sandbank Filtrate	45	10	8.3

On the other hand, a decrease in total DOCl as a result of ozonation is evident.

Another publication of Stieglitz (10) (figure 1) gives the changes of organic chlorine concentrations in water after different treatment steps. This study demonstrates a clear increase in GOCl and aliphatic chlorine and decrease in aromatic chlorine following ozonation.

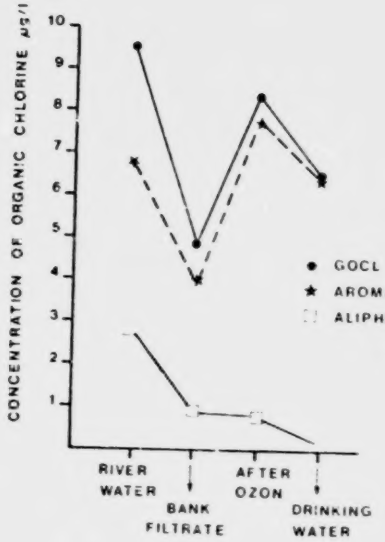


Fig. 1

Concentration of organic chloride after different treatment processes (13)

According to the authors of these publications the increase in certain chlorinated organic compounds following ozonation can be explained by a breakdown of chlorinated organic compounds with high molecular weights to molecules which can be detected and identified by available analytical techniques.

A study similar to those of Stieglitz et al. and Kühn et al. has been carried out by the authors at the National Institure for Water Supply in the Netherlands.

In this study the effect of ozonation under practical conditions in two treatment plants was observed.

The source of water in both cases is the river Rhine. The difference in treatment, however, is that the first plant uses bank filtration, in the second one the water is stored in an open reservoir with a mean residence time of 150 days. Before ozonation break point chlorination, coagulation and filtration are applied.

The objective of the study was to determine and measure quantitatively as far as possible the individual organic compounds. This was done according to the general layout shown in Figure 2.

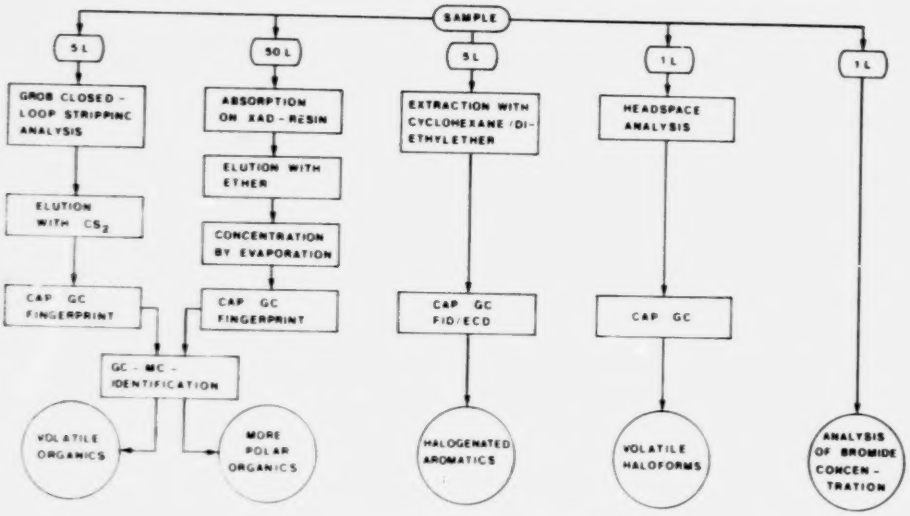


Fig. 2 Layout of the analyses of individual organic compounds and bromide

Details concerning the applied analytical procedures can be found in the annex.

In Table 3 the results of the analyses in relation to the first water treatment plant with bank filtration are tabulated.

TABLE 3 Organic compounds before and after ozonation in a water treatment plant using Rhine river water after bank filtration

Compound	Concentration (ng/l)	
	Before ozone	After ozone
chloroform	-	100
dibromochloromethane	-	100
bis(2-chloro-isopropyl)ether	2500	3000
1,2-dichlorobenzene	500	500
1,4-dichlorobenzene	200	200
1,3-dichlorobenzene	200	200
trichlorobenzenes	not present	not present
trichloroethene	-	300
tetrachloroethene	30	100
benzene	30	10
dibuthylphtahalate	300	3000

A striking feature in these data is the relatively high amount of bis(2-chloro-isopropyl)ether which is, as to be expected, not broken down by ozonation.

Furthermore, the observed increases of tetrachloroethene and trichloroethene should be noted. These increases have also been found by Stieglitz.

The di-butylphtalate is believed to be an artifact, originating from plastic tubes that are used in the treatment plant.

The situation in the second water treatment plant is shown in Table 4.

TABLE 4 Organic compounds before and after ozonation in a water treatment plant using Rhine water after open storage and chlorination

Compound	Concentration (ng/l)	
	Before ozone	After ozone
chloroform	10.000	10.000
dichlorobromomethane	13.000	12.500
chlorodibromomethane	3.000	10.000
dichloroiodomethane	-	1.000
bromoform	300	3.000
tetrachloroethene	300	1.000
bromochloroiodomethane (?)	-	300
chlorotoluene	30	10
hexachlorobutadiene	100	100
bis(2-chloro-isopropyl)ether	500	-
1,2-dichlorobenzene	100	100
1,4-dichlorobenzene	400	200
1,3-dichlorobenzene	200	200
1,2,3-trichlorobenzene	100	100
1,2,4-trichlorobenzene	100	100
heptanol	-	30
ethylbenzene	30	10
alcohol or ketone	30	300
alcohol or ketone	300	1000
alcohol or ketone	100	300

From the results of the analyses it can be noted that the use of breakpoint chlorination prior to ozonation has produced much greater concentrations of halogenated organic compounds than those found in the bank-filtered water.

As expected, most of the halogenated compounds are not or only slightly removed by subsequent treatment with ozone.

Since chloroform and dichlorobromomethane did not increase during ozonation, it is not likely that the rather drastic increases of chlorodibromomethane and bromoform are due to a prolonged action of the breakpoint chlorination. Therefore another mechanism must be involved.

What really strikes us from these results are the increased levels of brominated and possibly iodinated haloform compounds found after ozonation. Possible explanations for this phenomenon are discussed in section 5.

The oxidation of bromide to the already mentioned hypobromous acid is confirmed in Table 5.

TABLE 5 Results of the analyses of bromide

		Cl^- (mg/l)	Br^- (μg/l)
chlorination	before O_3	234	440
	after O_3	237	190
without Cl_2	before O_3	177	410
	after O_3	178	200

The bromide-ion concentration prior to ozonation was about the same in both cases (400 µg/l) and in both cases a 50 % reduction occurred as a result of ozonation.

5. General Considerations on the Mechanisms of Halogenation During Ozonation

The observed increases in haloforms and other halogenated compounds after ozonization are generally not to be considered as a result of halogenation, except for the brominated and iodinated compounds. Rather it must be regarded as an outgrowth of the incomplete analytical techniques currently available. There is no evidence that increased chlorination has occurred; rather it appears that non-observed chlorinated compounds have been rendered accessible to observation.

The increase in brominated and iodinated organic materials, particularly the halomethanes, is to be attributed directly to ozonation. Rook (1) has demonstrated formation of HOBr from Br^- in ozonation of Rhine water and has shown an increased bromine content in halomethanes formed on chlorination after ozonation. Determinations in the present study showed a decrease in Br^- content from 0.4 mg/l to 0.2 mg/l as a result of ozonation. Concurrently with this decrease, the increases in $CHBr_2Cl$ from 3 to 10 µg/l and in $CHBr_3$ from 0.3 to 3 µg/l in ozonation of a sample (Table 3) are noteworthy. Another possible explanation for these observations, advanced by Stieglitz et al., is that ozonation splits non-volatile chlorinated organic compounds into smaller volatile fragments that retain the organic chlorine originally present. This proposal is attractive in a general way, but is difficult to adapt specifically to substances like trichloroethylene and tetrachloroethylene without postulating some unlikely starting materials.

A similar but even more speculative proposal can be advanced with regard to changes in polarity of halogenated compounds rather than changes in molecular size, as the properties producing incomplete measurements of organic chlorine already in water before ozonation.

Chlorinated lower organic acids and amines are examples of materials that might be responsible for this phenomenon. The increase in extractable organic material at the expense of adsorbable dissolved organic chlorine observed by Stieglitz implies an elimination of water-solubilizing groups like OH, COOH and C=O. Once again, however, the increase in heavily chlorinated ethenes is not well explained.

A different type of explanation can be visualized if it is postulated that organic (or other) material in the original water can complex or otherwise interact with volatile chlorinated compounds to decrease their activity and thus make them less prone to volatilization or extraction. Then, when the complexing or restraining materials are broken up or made ineffective by ozonation, the chlorinated materials are released at full activity to give a greater response in analysis.

The necessary initial assumption may seem improbable, but so little is known of phenomena at the submicrogram per litre level that it ought not to be summarily eliminated. If it is valid, then the observed results with polychlorinated ethylenes follow almost automatically.

Finally, it may be noted that, if at any point in the complex sequences of reactions that may follow an initial ozonation step there occurs a nucleophilic displacement reaction with transitory formation of carbonium ions, then the high concentration of chloride in Rhine water provides an excellent opportunity for nucleophilic displacement by chloride rather than the normal reagent. In this event an increase in carbon-chlorine bonds would occur without intermediate occurrence of elemental chlorine or HOCl.

As an addendum to this mechanism it may be noted that displacement of the carbonbromine bond is normally much easier than displacement of a carbon-chlorine linkage. It is thus conceivable that, following the formation of tribromomethane according to the first mechanism, the reaction

$$Cl^- + CHBr_3 \longrightarrow CHBr_2Cl + Br^-$$

occurs subsequently by nucleophilic displacement. The possible mechanisms are once again summarized in Table 6.

TABLE 6 Possible mechanisms for observed increases in halogenated compounds on ozonation

1. $O_3 + Br^-$ (I^-) $\longrightarrow$ HOBr $\longrightarrow$ Br derivatives (I-deriv.)
   (Note: Br(.4 mg/l before) $\longrightarrow$ Br^- (.2 mg/l after)
2. O_3 splits non-volatile chlorinated compounds into smaller volatile chlorinated fragments
3. O_3 attacks polar spots in molecules to eliminate non-polar (adsorbable) chlorinated fragments
4. Ozonation breaks up complexing or adsorbing materials (fats, humates) that inhibit volatilization or extraction
5. Occurrence of any S_N1 nucleophilic processes in ozonation reactions would allow Cl^- substitution

6. Conclusions

From the results of this study and previous ones it is clear that the use of ozone during the preparation of drinking water can also result in the formation of halogenated compounds. Our study of the two water treatment plants in the Netherlands shows that such a production, particularly of brominated compounds, is enhanced in case chlorination precedes ozonation. The mechanism for this phenomenon probably involves intermediate production of bromine, but should be studied further.

A small-scale pilot plant, suitable for studying the mechanisms of reactions of oxidants in different types of water is being constructed at the Dordrecht facilities of the N.I.W.S.

The effects of individual oxidants, including U.V.-radiation as well as different combinations of them will be evaluated by identifying the products formed and by testing the mutagenicity of the oxidized water using different types of micro-biological screening tests.

ANNEX 1

Experimental

In order to measure halogenated compounds as completely as possible, four different concentration and separation techniques (head-space analysis, Grob stripping, Junk XAD-resin adsorption and cyclohexane extraction) were used on portions of the same samples. Subsequent analyses were carried out with specialized GC instruments and columns and also with GC-MS apparatus. In addition, bromide analyses were performed according to the Fishman-Skougstad method (11) as modified by Rook (2).

Head-space analyses were used for determination of very volatile substances, such as chloroform and trichlorethene. Sample portions of 0.4 l were mixed with 0.1 l N_2 in 500 ml closed vessels for 1 hour at 30°C. Head-space samples of 10, 100 and 1000 μl were then injected into the inlet of a TRACOR - 550 gaschromatograph with a 50 m capillary glass column coated with UCON and with a ^{63}Ni-EC detector.

Extraction with cyclohexane-ether was used principally for estimation of chlorinated aromatic compounds and haloforms with elimination of background interference of non-extractable substances. One litre portions of sample were extracted with equal volumes of a 1:1 cyclohexane-ether mixture. After the immiscible liquids had been shaken together vigorously in a separatory funnel, the liquid layers were allowed to separate and then portions of the upper organic layer, without concentration, were injected at the inlet of a VARIAN-1800/2000 gaschromatograph having a capillary column with OV 1 equipped with a Grob-splitter with double parallel detectors, 1 electron capture and flame ionization (12).

Grob stripping (13, 14) was carried out on 5 litre portions of sample that were maintained at 30°C in a closed-loop apparatus through which N_2 was recirculated for 2 hours at 2 litres per minute.

Vaporized organic compounds were collected on 10 - 20 µg of carbon powder. After stripping had been completed, adsorbed materials were eluted from the carbon with three successive 8 ml portions of CS_2. The eluates were combined to give a final total volume of about 20 µl, which was stored at -40°C until analyzed.

For analysis, a 1 µl portion of the eluate was injected into the part of a CARLO-ERBA 2101 gaschromatograph containing a 50 m glass capillary column coated with UV101; it was equipped with a flame-ionization detector.

For a more complete survey of higher-boiling and more polar compounds, concentration on XAD resins was performed according to Junk (15, 16). Fifty litres of a sample were passed upflow through 30 ml beds of 1:1 mixed XAD-4 and XAD-8 resin (Serva, Heidelberg) held in a 15 mm glass tube. The resins had previously been cleaned by repeated batch extraction with ether, ethyl acetate and ethanol; they were stored under ethanol. After the adsorption step was finished, the resins were extracted with successive portions of ether to a total volume of about 30 ml, which was subsequently reduced to 500 µl by evaporation at 0°C into a pure N_2 stream. One µl portions of this concentrate were analyzed with the same gaschromatographic equipment described in the section on the Grob method.

GC-MS analyses of the Grob and Junk concentrates were performed with a VARIAN gaschromatograph containing a 50 m, UV-101 coated, glass capillary column. The chromatograph was programmed for 5 minutes at 0°; then 3 minutes at 30°, followed by continuous increase at 4° per minute from 30°C to 180°C. The exit was connected to a Finnigan quadrupole mass-spectrometer with one second scan-time. This was coupled to a W.D.V. data system. Spectra were compared with the "Eight Peak Index" or, by telephone hook-up, with the U.S. E.P.A. data bank.

Bromide determinations were based on the catalysis by Br^-, or iodide oxidation by permanganate (11). After 5 minutes of reaction, the I_2 formed was extracted with tetrachloroethane and measured spectrophotometrically.

(1) ROOK, J.J.
J. AWWA 68 (1976), 168

(2) ROOK, J.J.
Het ontstaan van trihalomethanes bij behandeling van drinkwater met chloor
Dissertation L.H. Wageningen (1978)

(3) MONTIEL, D.
Les halométhanes dans l'eau. Mecanismes de formation, evolution, elimination
Dissertation l'Université P. et M. Curie, Paris (1978)

(4) CHIAN, R.S.K.
Identification of End Products from Ozonisation of Compounds Commonly Found in Water
AWWA, Research Foundation, Water Reuse Report 8 (1976), 13

(5) -
Einfluß der Ozonisierung auf organische Wasserinhaltsstoffe
Report F.J. Borrus & Cie., Boncourt (1976)

(6) SYMONS, J.M. et al.
Ozone, chlorine, dioxide and chloramines as alternatives to chlorine for disinfection of drinking water
E.P.A. Report (1977)

(7) EBERHARDT, M. et al.
gwf-Wasser/Abwasser 116 (1975), 6, 245-247

(8) KUHN, W. et al.
J. AWWA 70 (1978), 326

(9) SYMONS, J.M.
Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes in Drinking Water
E.P.A. Report (1976)

(10) STIEGLITZ, L. et al.
Vom Wasser 47 (1977), 347

(11) FISHMAN, M.J., SKOUGSTAD, M.W.
Anal. Chem. 35 (1963), 146

(12) PIET, G.J. et al.
A fast quantitative analysis of a wide variety of halogenated compounds in surface-, drinking- and groundwater
Internat. Symp. on the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, Toronto, May 1978

(13) GROB, K. et al.
J. of Chrom 106 (1975), 299-315

(14) GROB, K. et al.
J. of Chrom. 117 (1976), 285

(15) JUNK, G.A. et al.
J. of Chrom. 99 (1974), 745

(16) JUNK, G.A. et al.
Z. Anal. Chem. 282 (1976), 331

NOTE ON THE HALOFORM FORMATION POTENTIAL OF PRE-OZONIZED WATER

J. Hoigné

The papers given at the conference about the effect of a preliminary ozonization on the subsequent chlorination processes show clearly that the action of ozone can depend on a wide variety of reaction and water parameters. This corresponds fully to what we have come to expect in the light of the present-day knowledge of the kinetics of ozonization processes. We should like to propose the following hypothesis for discussion: depending on the performance of the ozonization, the water constituents are predominantly oxidized by direct ozonolysis or by secondarily formed $OH^{\bullet}$ radicals [1]. In the example of the oxidation of an aromatic ring system the two types of reaction lead to different intermediate products (Fig. 1). Ring cleavage is mainly expected in ozonolysis, with the formation of dicarboxylic acids, such as oxalic acid, in subsequent steps. In these cases enrichment of trihaloform precursors in the water need hardly be reckoned with. However, the proportion of ozone that decomposes in water to $OH^{\bullet}$ radicals oxidizes aromatic ring systems via hydroxylation to hydroxycyclohexadienyl radicals, which give hydroxy-substituted benzenes (phenols, resorcinols etc.). Compounds of this kind are known to be particularly reactive trihaloform precursors. If the ozone reaches the reaction centre before it decomposes, these compounds are rapidly oxidized further by ozone. In the opposite case, it is to be expected that compounds of this type will be enriched in the water and on subsequent chlorination will lead to an increased formation of trihaloforms.

If methyl-substituted olefins are present in the humic substances, it can be expected that they will be oxidized to

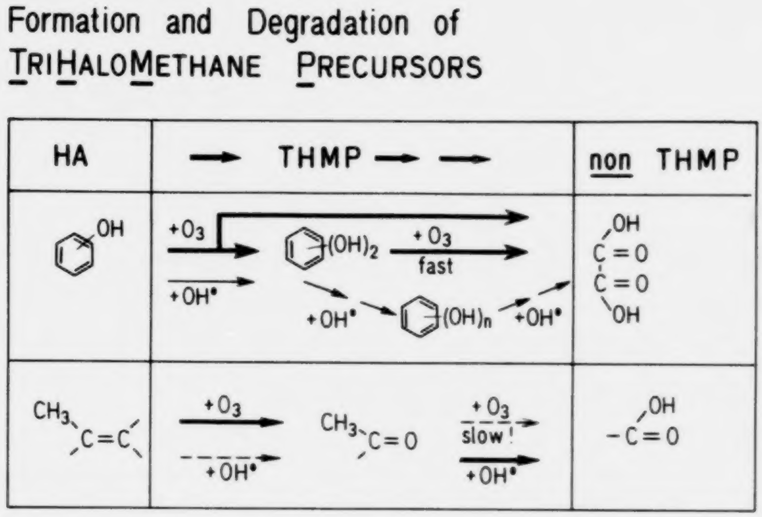


Fig. 1 Dependence of the product formation on the performance of the ozonization process [2]

methyl ketones by direct ozonolysis [1]. However, many of the methyl ketones are extremely stable to ozone [3]. They can also be enriched in the water until they are oxidized further by secondary OH˙ radicals. This means that the formation and degradation of methyl ketone-like haloform precursors proceeds in accordance with laws quite different from those governing the formation of phenol- or resorcinol-like trihaloform precursors [2].

Whether the ozonization-initiated oxidations proceed via direct ozonolysis or via previously formed hydroxyl radicals depends not only on the nature of the substrate molecules but also on the nature of the ozonization process. Fig. 2 shows that the time during which an ozone molecule is available for direct reaction is limited by the rate at which it breaks down into radicals. This rate is known to increase with rising pH. However, since the decomposition of ozone proceeds in addition by a chain reaction in which radicals

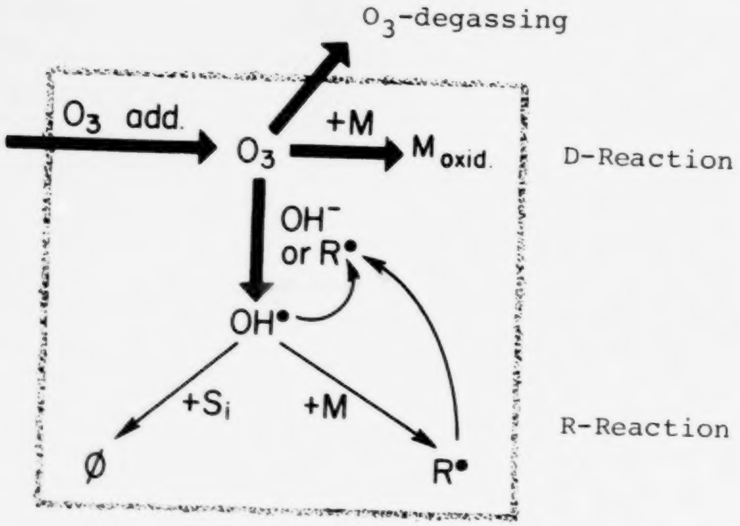


Fig. 2 Dependence of the type of oxidation on the performance of the ozonization process [3]
M: Oxidizable water constituents
S: Scavengers
$R^\bullet$: Free radicals

function as chain carriers, many water constituents are also decisive for the decomposition rate of the ozone [4]. Thus, certain organic constituents (e.g. benzene in the 0.1 mg/l range) lead to an accelerated ozone decomposition. Other constituents, such as bicarbonate ions or aliphatic alcohols, inhibit the chain reaction by abstracting radicals from the process [4]. This gives rise to the situation that the ratio of the direct ozonolysis to the radical $OH^\cdot$ oxidation is influenced by a wide range of constituents present in the water. On the basis of the chain reaction accelerating the ozone decomposition, it can also be understood why the kinds of reaction can depend on the istantaneous local ozone concentration, i.e. also on the way in which the ozone is introduced.

If the results of ozonization processes are to be comparable, an ozonization must be described very carefully. It therefore seems to us to be very important that the greatest attention be focussed on a careful establishment of the process arrangements and characterization of the water. If this is not done, the experience cannot be generalized or extended to other situations.

(1) HOIGNE, J., BADER, H.
Ozonbedarf und Oxidationskonkurrierwert verschiedener Wassertypen bezüglich der Oxidation von Spurenstoffen (this publication)

(2) HOIGNE, J.
Discussion of paper by M. Doré on "Influence of oxidizing treatment on the formation and the degradation of haloform reaction precursors"
Prog. Wat. Tech. 10 (1978), discussion part, in press

(3) HOIGNE, J., BADER, H.
Kinetik und Selektivität der Ozonung organischer Stoffe in Trinkwasser
Wasser Berlin '77, Tagung der Fachgruppe Wasserchemie in der GDCh, Colloquium Verlag Berlin (1978), 261-276

(4) HOIGNE, J., BADER, H.
Beeinflussung der Oxidationswirkung von Ozon und OH-Radikalen durch Carbonat
Vom Wasser 48 (1977), 283-304

THE CONDITIONS OF OZONIZATION

J.P. Legeron

The number of studies and investigations on ozone and the number of cases of the practical application of this gas become greater every day.

However, the results obtained seem to be very variable,which is perhaps in many cases due to omissions or errors, but perhaps also to the absence of a common language.

In actual fact the aim of ozonization and the conditions of the use of ozone could not be interlinked more closely. Ozone is a chemical substance and as such reacts with other species present in an aqueous medium: we can therefore speak of oxidation kinetics and thus of conditions for maximum reaction rates.

The temperature and sometimes also the pH of the water are difficult to change, but the ozonization parameters are really easily modified:

This is the situation, for example, with the ozone concentration in the carrier gas, with the dose used for the treatment, with the contact time, with the residual ozone concentration in the gaseous and liquid phases, and with the lifetime of this residual ozone in water.

The ozone can be added in one portion or in several portions and at one or more points in the treatment line.

The contact can be intermittent or continuous. Many studies, for example that by Monsieur Chedal at the Berliner Wasserkongress in 1977, have indicated the influence of these conditions.

Let us first of all disregard the case of disinfection with ozone, which is not the object of this symposium. Suffice it to say that in this case the maintenance of a certain quantity of dissolved residual ozone for some minutes makes it possible to enhance the organoleptic properties of the water, a fact that is attested by the readiness of ozone to react with some substances still present in the medium.

While these reactions proceed relatively slowly, this is not the case during the oxidation of very many organic and inorganic compounds. Depending on the type of the water, the ozonization serves a different purpose at the start and sometimes in the middle of the treatment chain.

The case in question may be, for example, the oxidation of iron and manganese, and here the contact times are short and the doses depend on pollution of the water.

In other cases we may be concerned with an improvement of the flocculation; for this both the contact time and the dose must normally be small.

Finally, we may be aiming at improving the biological degradation. In this case the dose can be made higher, to introduce oxygen into the water and to improve the bio-degradability of the substances present.

Each case has its special features and for this reason relevant trials must be performed either in the laboratory or, better still, in a pilot plant.

These trials must be as comprehensive as possible before any qualitative or quantitative conclusions may be drawn.

Without going into the details of the process, which has already been the subject of several contributions, I should like to conclude with two specific examples.

- The first relates to the oxidation of manganese in a French river water:
  at constant contact time, quadruplication of the ozone concentration before it is added makes it possible to reduce the treatment dose and therefore the ozone production by almost 50%.

- The second and last example relates to the oxidation of an iron/silica compound in a ground water of African origin:

  splitting of this complex and the oxidation of the iron thus released cannot be achieved in a single ozonization step even with a high dose and a long contact time; the solution was found in several consecutive small additions of ozone alternating with aeration phases.

  This confirms that the results can be positive or negative, depending on the ozonization conditions.

DESCRIPTION OF REACTIONS BY GROUP PARAMETERS

H. Lienhard and H. Sontheimer

In this report I should like to discuss in greater detail a problem that keeps recurring in the study of ozone processes, namely how the changes caused by ozonization can be detected and described.

The possibilities existing today for this purpose should be discussed in the light of the experimental results obtained in studies on the optimal ozone input, on which Prof. Sontheimer spoke in his lecture on Monday. Briefly, such studies are aimed at establishing whether the ozone should be added in stages, e.g. in a sufficiently large reaction vessel by fine-bubble aeration, or whether it is more expedient, as possibly with a rotor, and then with an initially high concentration to allow the reaction to proceed slowly.

To provide practical data from the results of these studies, humic acids were used as model substances in the experiments. This gave rise to the problem that the chemical structure of humic acids is largely unknown and that during ozonization they form products not directly accessible to analysis. This means that the reaction of the model humic acid with ozone cannot be followed directly, so that the products formed must be characterized by measuring some accessible parameters.

To this end we used the 6 parameters shown in the left-hand column of Table 1.

We shall now describe how conclusions can be drawn, from the results obtained with these parameters, about the nature of the reaction products and about their effect on the treatment.

TABLE 1 Description of reactions by group parameters

Parameter	Measurable effect with stepwise addition of ozone as opposed to a single addition	Interpretation of the effect
Spectral absorption coefficient at 254 nm	Decrease	Degradation of the double bond system
DOC	No difference	No increased CO_2 formation
Flocculation effectiveness	Improved relative flocculation activity	More polar molecules
Molecular weight distribution	Displacement of the mean molecular weight towards smaller values	Smaller molecules
Adsorption on $CaCo_3$	Displacement of the isotherms to the left	More polar groups on the molecule
Haloform formation potential	Less trihalomethanes	Degradation of the electrophilic centres, fewer double bonds

The middle column shows the effect measured for the parameter on the left, obtained with fractional addition of the ozone. The right-hand column lists the conclusions that can be drawn from this about the change in the organic substances.

From the observed decrease in the spectral absorption coefficients at 254 nm we concluded an intensified degradation of the double bond system with intermittent ozone input. The fact that the DOC is the same for both modes of ozone input means that only a different change in the humic substances occurs, which also happens in practice, since the effectiveness of flocculation is enhanced by stepwise ozone addition, as shown in Fig. 1.

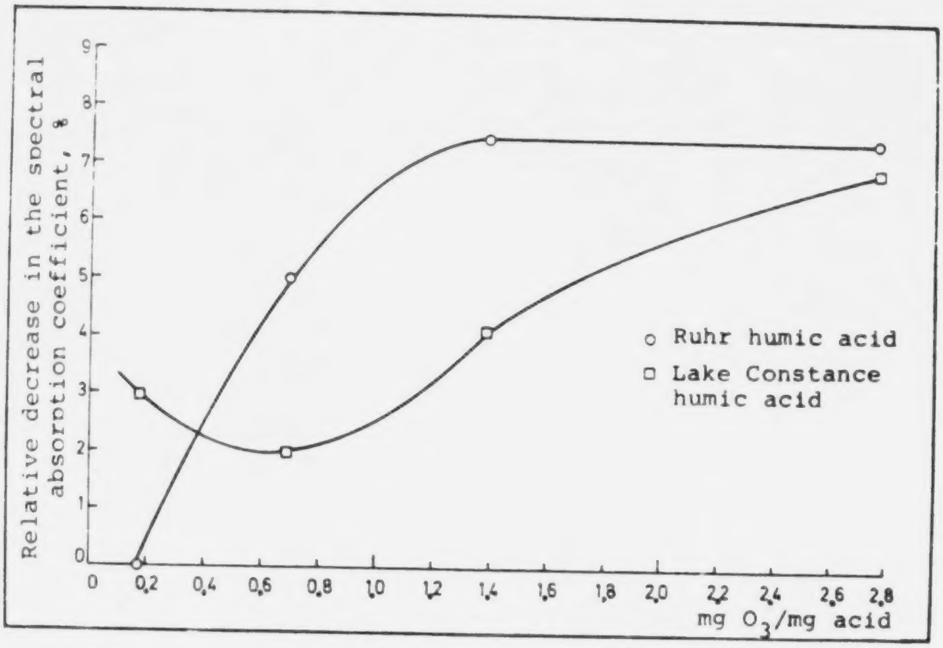


Fig. 1 Relative improvement of flocculation effectiveness by stepwise ozone addition for two humic acids

This figure illustrates the relative improvement of the flocculation effectiveness due to the intermittent ozone input. It can be seen that e.g. for the Ruhr humic acids after stepwise ozonization by flocculation alone the spectral absorption coefficient is reduced by up to 7.5% more than in the case of a single addition. The same applies to the humic acid from Lake Constance.

To understand this effect the molecular weight distribution must be measured, as can be seen in Table 1. The distribution is displaced towards smaller molecular weights. The absorption experiments additionally performed on $CaCO_3$ confirm an increase in polar groups compared to the case of the single addition of ozone. The haloform formation potential is also reduced (Fig. 2).

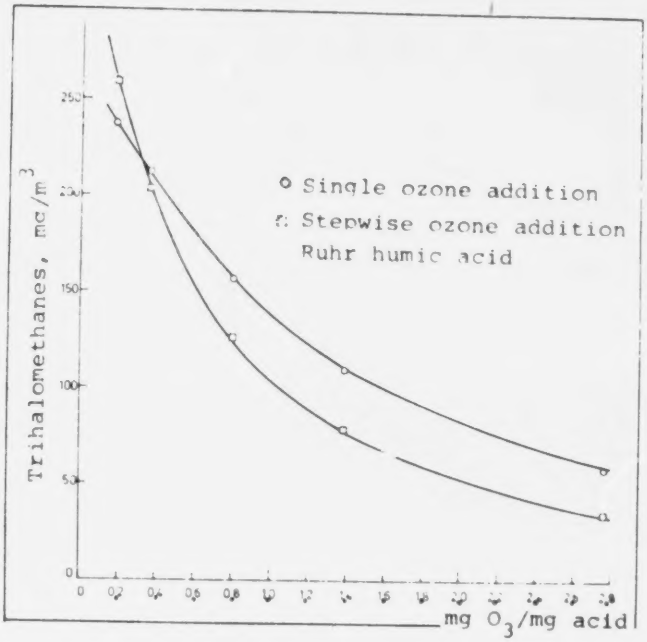


Fig. 2 Dependence of the haloform formation potential on the amounts of ozone for two different kinds of ozone addition

The figure shows the amounts of trihalomethanes formed during the chlorination as a function of the ozone input. From the course of the curves it can be seen that stepwise ozone addition reduces the haloform formation potential more strongly, and this indicates that fewer electrophilic centres and so fewer double bonds are available to the electrophilic attack of the chlorine when this type of ozonization is used.

If the information yielded by each individual parameter listed in the right-hand column of Table 1 is compared, it can be seen that the data provided by each parameter are supported by the other results.

For example, the results of the flocculation experiments can be explained both by the change in the molecular weight distribution and by the increase in the concentration of polar groups. The two effects run in opposite directions and lead to an explanation of the different behaviour in the two modes of ozone addition.

Without going into further detail of all the interesting relationships, from the results presented it can be concluded that a combination of a number of experimental parameters can lead to a better appreciation even of small effects and to a deeper understanding of the processes taking place during ozonization.

PRODUCTION OF OZONE FROM OXYGEN

G. Uhlig

The problem appears trivial: a molecule consisting only of oxygen atoms can likewise only be produced from oxygen. The production of ozone from air succeeds only because, in spite of environmental loading, even in regions of accumulation, air always contains 21 vol-% of oxygen.

However, it is also this oxygen concentration that finally limits the yield and the efficiency of even the best ozone generators. This applies above all when not only the amount of ozone produced but also the ozone concentration achieved is the main criterion, because the dissolution of ozone in water is subject to the Henry-Dalton law, according to which the solubility of ozone is proportional to its partial pressure, and thus to its concentration, in the gas phase.

According to the laws of reactions kinetics, there is no doubt that the yield and efficiency of the production of any material increase with the increasing concentration of the starting components. Some measurements, here cited only as examples, for series-connected ozone generators, dimensioned for the production of ozone from air illustrate this point better than the corresponding reactions and equations:

Fig. 1 shows, on the basis of Masschelein's measurements (1), the increase in the hourly production of ozone with increasing oxygen concentration at a constant gas throughput for various power levels of an ozone generator. At the same time, as can be seen in Fig. 2, the energy expenditure on the production of 1 g of ozone is greatly reduced.

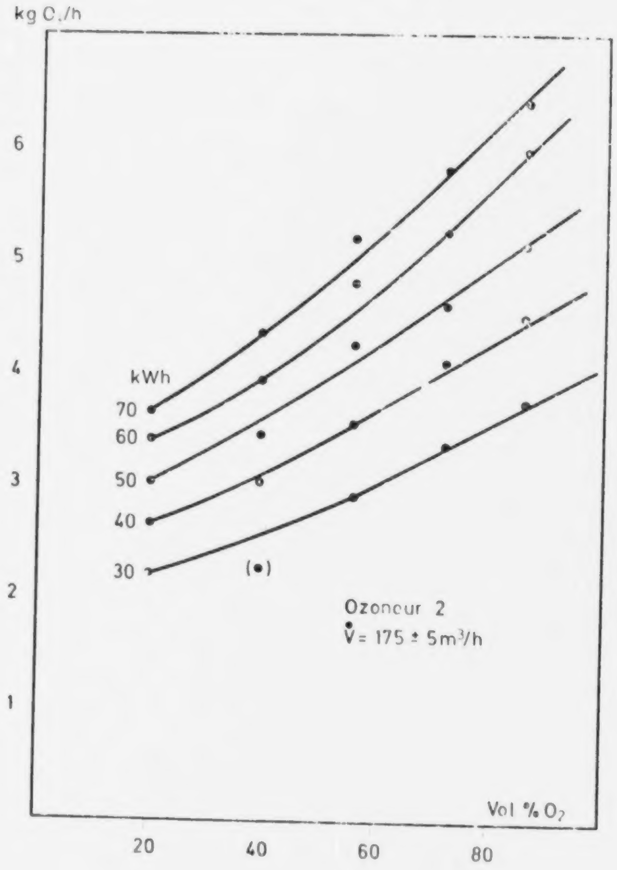


Fig. 1 O_3 production/h in dependence on the O_2 concentration.
(after W. Masschelein, T.S.M.
L'EAU 71 (1976) 385)

Ozoneur = ozone generator

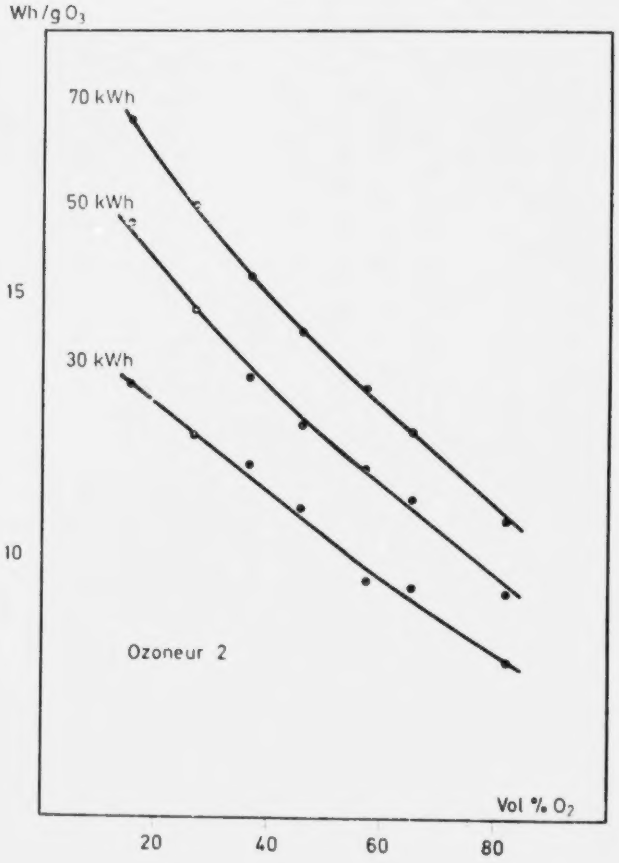


Fig. 2 Specific energy requirement of O_3 production in dependence on the O_2 concentration.
(after W. Masschelein, T.S.M.
L'EAU 71 (1976) 385)

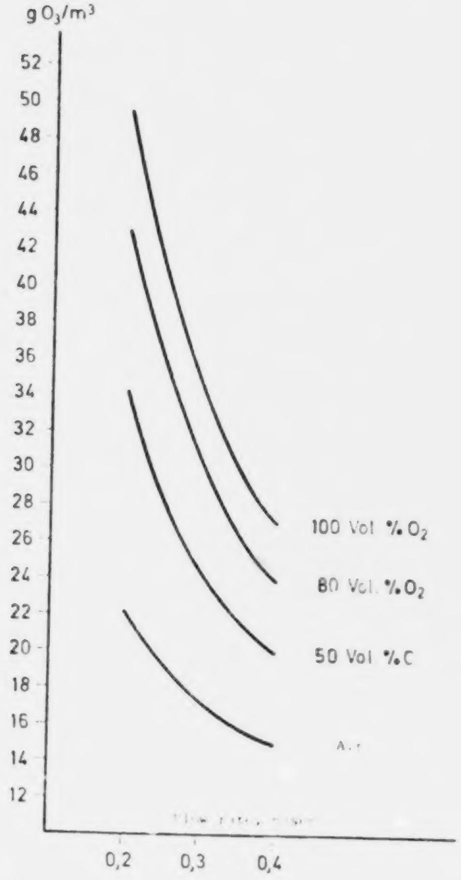


Fig. 3

O_3 concentration produced in dependence on the gas flow at various O_2 concentrations. (after M. Bredtmann, Wasser, Luft und Betrieb 11(1974) 605)

Higher concentrations of ozone are generally achieved by reducing the gas throughput of the ozone generator. Fig. 3 shows a diagram taken from Bredtmann (2), in which the concentrations of ozone obtained with a series-connected tubular ozone generator during the change-over from air to pure oxygen is demonstrated.

Here too, as can be seen from Fig. 4, the specific energy expenditure for the production of increasing ozone concentrations on going over from air to pure oxygen is essentially reduced.

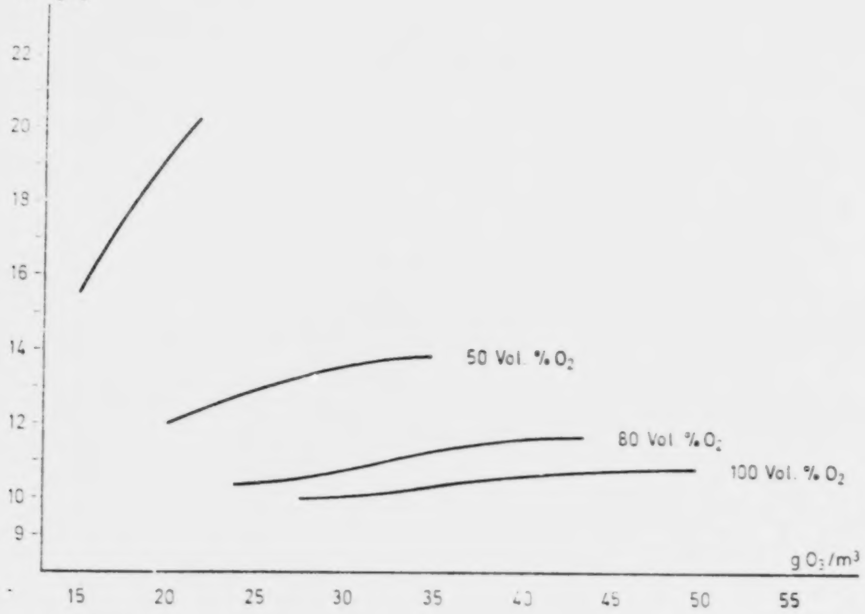


Fig. 4 Specific energy requirement in dependence on the O_3 concentration produced at various O_2 concentrations. (after M. Bredtmann, Wasser, Luft und Betrieb 11(1974) 605)

Even when the starting gas contains only 50 to 90 vol-% of oxygen it is an additional advantage for the dissolution of ozone in water that the correspondingly smaller proportion of nitrogen still permits a gasification of the water under pressure, which in the case of ozone production from air would lead to supersaturation of the water with nitrogen.

However, all these advantages do not cover the costs of the oxygen consumed if this is not returned to the production after the ozone has been washed out. Therefore, if the process is to be economically viable, gas circulation must be installed. On account of the improved ozone dissolution, however, only a partial water stream needs to be gasified with ozone for this purpose, and expensive structures and installations for the gasification of the whole amount of raw water become unnecessary.

By means of the production of high ozone concentrations in the gas phase (50-90 ozone/m^3 is nowadays a realistic figure) and by the use of pressure in the gasification of the water in space-saving scrubbers or columns, ozone concentrations of 20-80 g/m^3 of water can be reached. Accordingly, the dissolution of 2-3 g of ozone per m^3 of raw water still requires only the gasification of a partial water stream amounting to 3-10% of the total water. The highly concentrated partial stream is then mixed with the main stream in such a way as to ensure a good distribution and a sufficient reaction time.

The apparatus and the physico-chemical principles of this process have already been given in detail by Axt (3) 1958 in his dissertation "An indirect process for the ozonation of water". This already included calculations for the design of ozone-introduction columns, calculations of the energy yield during the production of ozone from oxygen, and a description of a specialized ozone generator to be operated at 6-7 bar that provides for gas circulation at a constant excess pressure. Since such ozone generators are not produced commercially, the gas circulation must in practice be operated with two pressure levels: an optimal pressure for the dissolution of ozone and an optimal pressure for the production of ozone, which in the majority of cases is restricted to 1.6 bar with today's ozone generators.

A large-scale realization of the process took place 8 years later for the first time at the Duisburg AG municipal works with an ozone plant designed for a throughput of 2500 m^3 of raw water per hour. This plant was commissioned in 1966 in the Wittlaer waterworks for the treatment of Rhine water filtrate. Simon and Scheidtmann (4) 1968 have reported in detail on the extensive preliminary trials on adaptation of the process and on the technical data of the main plant.

The process scheme of this plant is given in Fig. 5: fresh oxygen is led out of a 5000 m^3 liquid oxygen tank (bottom left in the figure) via an evaporator warmed by air and directed to the gas circulation before the production of ozone. The ozone production at 1.05 bar in 4 tubular ozone generators (only one unit is shown in each case) supplies an ozone concentration of 40-60 g/m^3. The pressure is then raised to 1.8 bar and the gas mixture 2 is conveyed to the ozone scrubbers, made in the form of packed columns, in which the partial stream of water - about 10% of the whole water treated - trickling in countercurrent through Raschig rings undergoes gasification.

The unconverted mixture leaving the scrubbers at the top is directed to a drying plant with a cooled condensate separator and returned for use in the production of ozone.

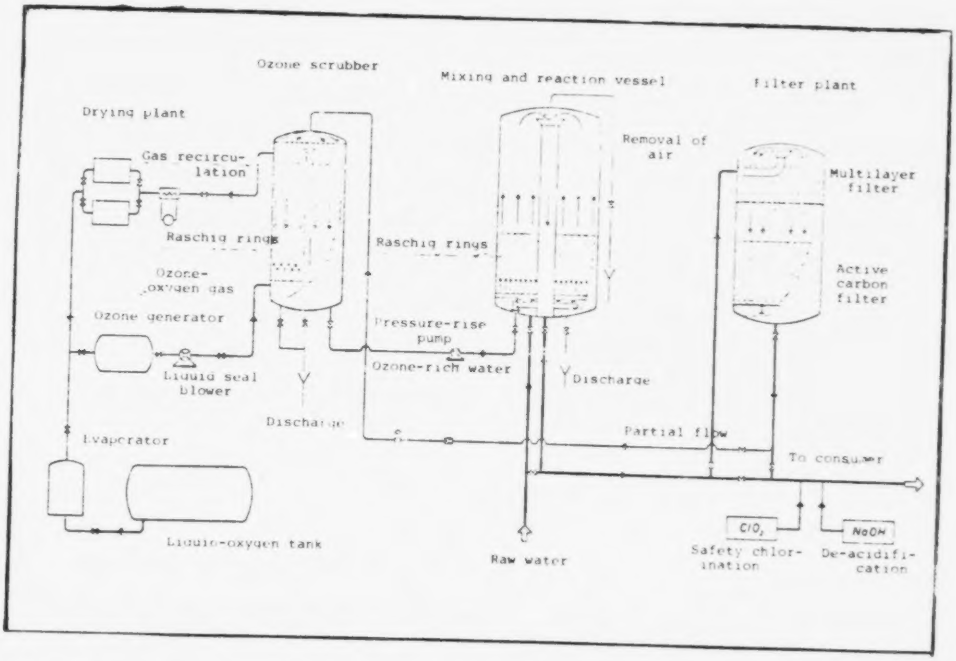


Fig. 5 Diagram of the ozone plant at Wittlaer Waterworks III

The partial stream of water, containing 10-25 g of ozone/m^3 and described in the diagram as "ozone-rich water" is added to the raw water in two reaction tanks after the pressure has been raised to 8 bar. The ozonized raw water coming out at the bottom through a concentric drainage funnel passes 20 two-stage filters with a total filter area of 206 m^2 per stage, consisting of a multilayer filtration for the removal of the flocculated ozone-oxidized products and an active carbon stage, connecting safety-chlorination with chlorine dioxide and deacidification with a solution of caustic soda.

The external appearance of the Duisburg ozone plant is illustrated in

Fig. 6, which shows the two scrubber columns for the dissolution of ozone and the pumps for increasirg the pressure,

Fig. 7, which shows the control panel, the ozone generators (right), and the reaction tanks (left) in the background, and

Fig. 8, which shows an external view of the whole plant.

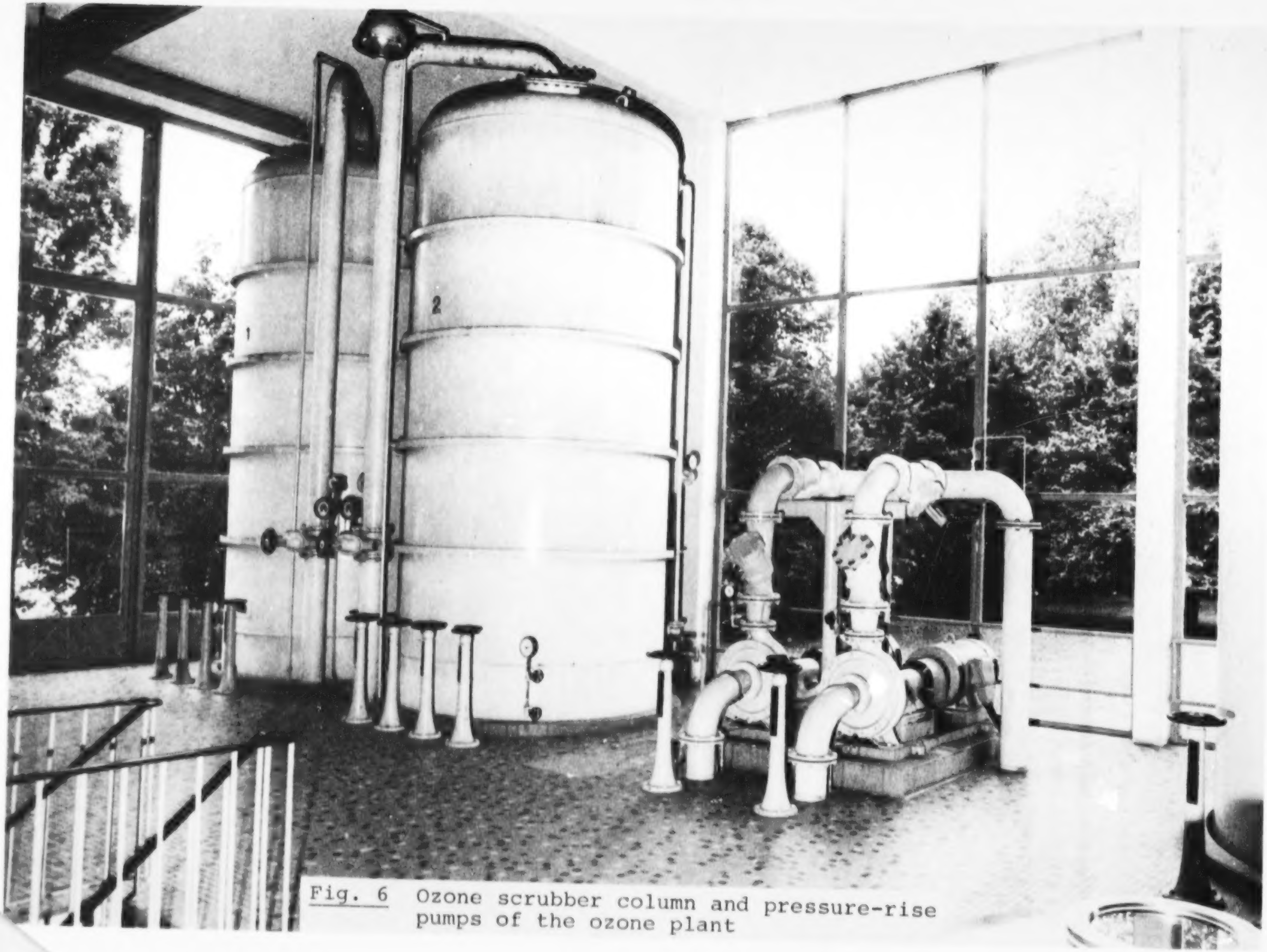


Fig. 6 Ozone scrubber column and pressure-rise pumps of the ozone plant

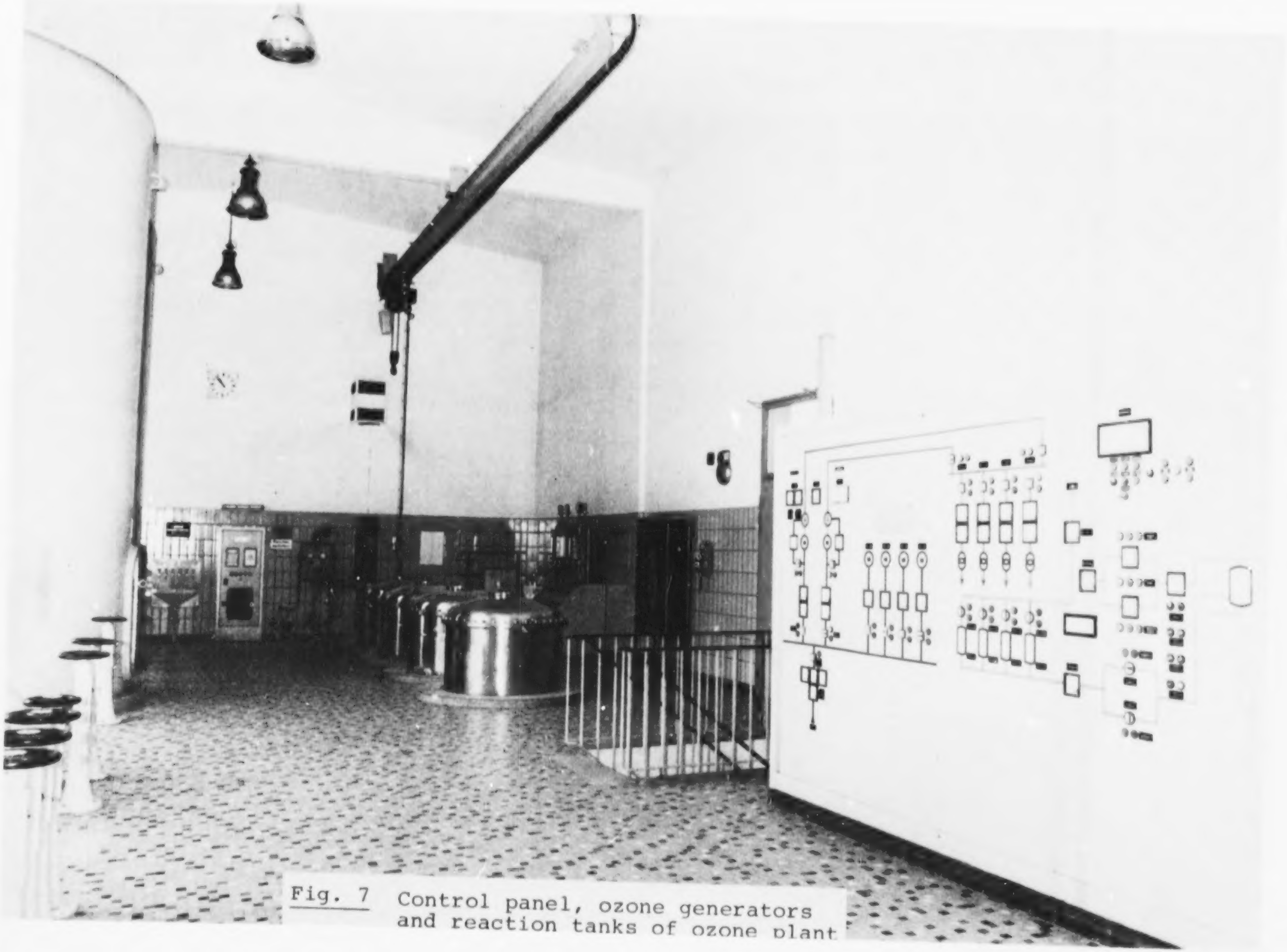


Fig. 7 Control panel, ozone generators and reaction tanks of ozone plant

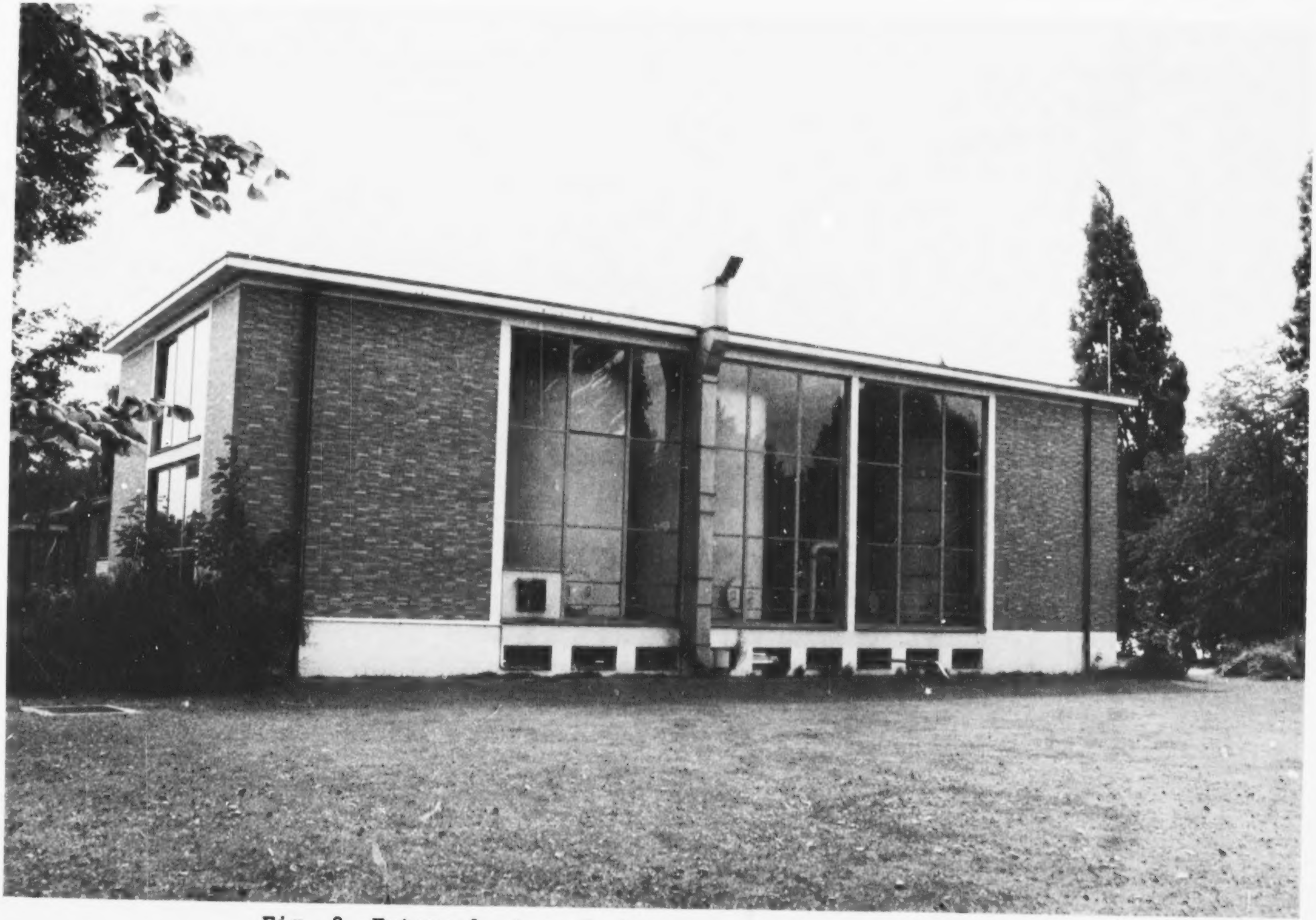


Fig. 8 External view of the ozone plant

Control of the ozone production only by the tension in the ozone generators at constant gas throughput is not optimal, since the ozone concentration is then diluted again.

However, the control also of the amount of gas in circulation, with the ozone concentration regulated to a constant value, already envisaged in this plant, has not been approved in the proposed form and is the object of further improvements, as is the design of the columns.

It should be emphasized that in this process the raw water from the feed pumps of the wells onwards undergoes the whole treatment already under distribution pressure, and the pressure need not be reduced for the ozone treatment.

In the selection of the pressure for operating the columns it must be remembered that the Henry-Dalton law applies not only to dissolution of the gases - this concerns above all oxygen in addition to ozone - but also to the release of gases dissolved in the water. The main component dissolved is still nitrogen, corresponding to its partial pressure in the air. However, in a pure oxygen/ozone mixture the partial pressure of nitrogen is zero, and thus does not correspond to the distribution equilibrium. Consequently, a partial pressure of nitrogen corresponding to the nitrogen content of the water is rapidly set up in the gas circulation by outgassing. The concentration corresponding to this partial pressure depends on the partial pressure of the oxygen and therefore on the selected total column pressure, which in turn determines the dissolution of oxygen in the partial stream of water.

These relationships are presented in Fig. 9 for nitrogen-saturated water in an easily followed diagram due to Albrecht (5): when the pressure is raised to 8 bar the nitrogen content in the gas circulation can be reduced to about 10%. As shown by measurements carried out by Rosen (6), and also by Cromwell and Manley (7), a smaller content of nitrogen scarcely improves the ozone production efficiency, and furthermore, increasing the pressure also reduces the column layout and dimensions. According to Greiner and Grünbein (8,9), at 5-7 bar 8-10 theoretical plates are necessary for almost quantitative washing out of the ozone.

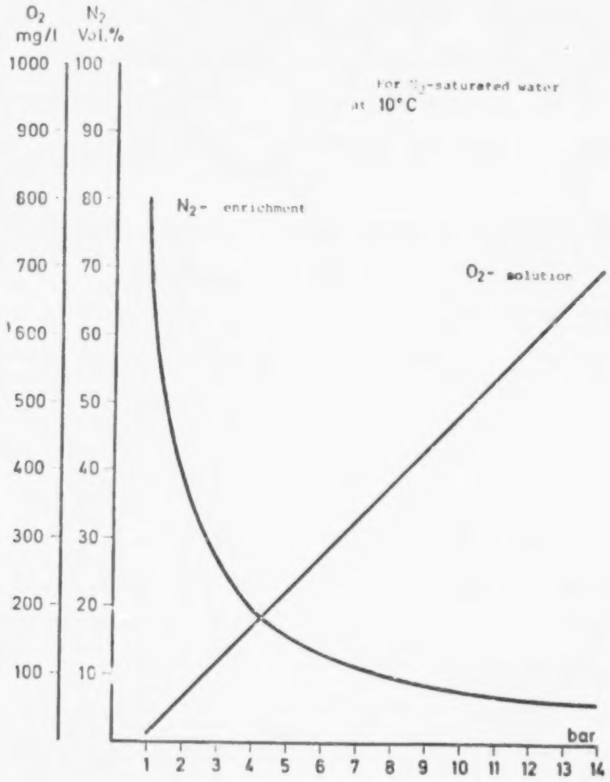


Fig. 9 Distribution equilibrium of nitrogen (vol-%) in oxygen and of oxygen (mg/l) in water (after E. Albrecht, Dechema - Monogr. 75 (1974) 343)

The pressure elevation is however restricted by the increasing oxygen dissolution, the limit being determined by the oxygen content and the ozone consumption of the raw water and also by the oxygen demand of the after connected treatment plant. To avoid this situation by a subsequent aeration of the water to drive out the excess oxygen necessitates considerable additional expenditure and is not practicable for a water treatment under distribution pressure in a closed system.

For open plants, on the other hand, even a slight enrichment of the aerial oxygen, without using gas circulation but with the pressure produced by the greatest possible depth of immersion of the gasification, can have certain advantages, as reported by Masschelein (1) and by Rosen (6).

For oxygen enrichment of the air Rosen (6) recommends a "pressure swing oxygen enrichment" with the use of a molecular sieve in 2 towers which are run alternately under different pressures.

Summary

1) With the same energy consumption of the ozone generators at least twice the amount of ozone per hour can be obtained, in at least twice as high concentration, when the ozone is produced from oxygen and not from air.

2) Corresponding to this increase in concentration, the ozone dissolution also increases for all types of gasification of the water, and on an additional application of pressure in suitable columns the dissolution is higher by a factor of 10-30 than in the case of open gasification of the water with ozone produced from air.

3) It is thereby possible to limit the gasification with ozone to a partial stream of water amounting to 3-10% of the raw water to be treated.

4) Since the oxygen is circulated none of the remaining ozone need be wasted. The ozone is almost completely dissolved or goes to the return gas.

5) At most 1/10 of the amount of gas that must be transported and dried in the case of ozone production from air is conveyed to the gas circulation in the case of production from oxygen. This reduces the costs of gas drying and transportation, together with the energy balance for ozone production and costs of cooling the ozone generators.

6) In the Duisburg process of ozonization of the drinking water, which is based in its concept on Axt's fundamental work (3), these advantages were already realized 12 years ago corresponding to the state of technology at that time. So far it has been the only conceivable process for ozone treatment of the water under distribution pressure in a closed system, and work on its improvement is continuing.

(1) MASSCHELEIN, W.
Perspectives de l'ozonation de l'eau au départ d'air enrichi en oxygène
T.S.M.L'EAU 71 (1976), 385-399

(2) BREDTMANN, M.
Bildung von Ozon und Konsequenzen für die Konstruktion von Ozonerzeugern
Wasser, Luft und Betrieb 18 (1974), 605-609

(3) AXT, G.
Über ein indirektes Verfahren zur Wasserozonisierung und dessen apparative und physikalisch-chemische Grundlagen
Dissertation Universität Karlsruhe (1958)

(4) SIMON, M., SCHEIDTMANN, H.
Die neue Ozonanlage der Stadtwerke Duisburg
gwf-Wasser/Abwasser 109 (1968), 877-882

(5) ALBRECHT, E.
Die Anwendung von reinem Sauerstoff für die Wasserbehandlung
Dechema-Monogr. 75 (1974), 343-356

(6) ROSEN, H.M.
Ozone Generation and its Economical Application in Wastewater Treatment
Water and Sewage Works 119 (1972), 114-120

(7) CROMWELL, W.E., MANLEY, T.C.
Effect of Gaseous Diluents on Energy Yield of Ozone Generation from Oxygene
Ozone Chemistry and Technology, Washington (1972), 304-312

(8) GREINER, G., GRÜNBEIN, W.
Gewinnung von Prozeßwasser aus Abwasser
Dechema-Monogr. 75 (1974), 399-406

(9) GRÜNBEIN, W.
Ozonisierung von Abwasser
Chemie-Ingenieur-Technik 46 (1974), 339

MEASUREMENT OF THE OZONE-DEMAND

C. Gomella

A - INTRODUCTION

The doses of ozone applied to pre-treated water, i.e. introduced into the ozonization reactor, which appear in the bibliography are difficult to compare with one another, and those used in laboratory trials cannot as a rule be extended to industrial practice.

The doses of ozone giving the same end result can vary considerably as a function of the experimental conditions and the experimental or industrial apparatus used. This is due to the fact that the ozone can be broken down as follows:

$$T = D + r + A + p$$

where T is the dose of ozone introduced into the reactor,
D is the amount of ozone actually used up in the various reactions (the ozone-demand),
r is the residual free ozone maintained in the water within the reactor (entrained by the water issuing from the reactor),
p is the ozone lost by entrainment with the exhausted ozonized air leaving the reactor,
and A is the ozone consumed through auto-decomposition.

A technical and economical analysis of an ozonization process, such as the application of a laboratory or pilot result, cannot be undertaken without a reasonably precise knowledge of the elements making up the treatment dose T. The problem is a complicated one, for these elements are not all independent of one another; in particular:

D is a function of the quality of the water, the time of the treatment, the value of the O_3 residue, and of the concentration of the ozonized air.

r is imposed by the investigator as a function of the desired result and also as a function of its effect on D and A.

A is dependent on quality of the water, the duration of treatment, r, and the concentration of the ozonized air.

p is dependent on the internal structure of the reactor and on the concentration of the ozonized air.

The present communication outlines a method used in France for fifteen years by the author and his associates, developed specially to surmount problems of interpretation. From a pragmatic point of view, this method has proved very effective and has enabled experimental results to be transposed to industrial conditions with a good degree of precision.

B. PRINCIPLE

When the amount of ozone actually introduced into the water has been determined, D and A are calculated by measuring $r_{(t)}$ at different times.

Before the calculation can be made, a hypothesis about the form of the auto-decomposition law must be formulated. The many studies mentioned in the bibliography give various formulations, notably 2nd or 3/2-power laws. In practice, it has been shown that a law of the form:

$$\ln \frac{r_o}{r} = a(t - t_o) \qquad a < 0$$

where ln is the natural logarithm,
r_o is the residue at time t_o,
r is the residue at time t,
and a is the auto-decomposition coefficient, is quite sufficient in current practice in the case of slightly polluted water with the usual pH (6 to 8). Without wishing to give a rigorous scientific meaning to this law, it appears that its application in the given case enables one to arrive at predictions and calculations of industrial installations.

It should also be noted that the method is not specifically connected with this form of the law, and that it is sufficient to replace the chosen law by one determined experimentally and better adapted to the case in question: $r = f(a,t)$, to be able to apply the method in its principle by simply modifying the mode of the calculation.

C. THE DIFFERENT STAGES OF THE METHOD

A quantity of ozonized air of a known concentration and a quantity of water are introduced into the same flask, after which they are stirred vigorously and the residual ozone is measured at successive moments in time.

Two measurements are sufficient to determine the auto-decomposition coefficient, that is, r_1 at time t_1 and r_2 at time t_2 :

$$\ln \frac{r_o}{r_1} = at_1$$

(t_o is taken to be the time origin)

$$\ln \frac{r_o}{r_2} = at_2$$

whence:

$$a = \frac{\ln \frac{r_2}{r_1}}{t_1 - t_2}$$

and

$$r_o = r_1 \, e^{at_1}$$

The ozone demand D can then be determined, provided that the initial concentration of the ozone introduced into the water (C_o) is known:

$$D = C_o - r_o.$$

C_o is easily calculated from the respective volumes v and V of the ozonized air and the treated water, from the ozonized air concentration, and from the distribution coefficient S (Henry's law) of the ozone between the air and the water at the temperature of the experiment, which is conducted under atmospheric pressure:

$$C_o = \frac{c\ v}{\frac{v}{S} + V}$$

If t is the time of the ozone treatment in the reactor, and r is the residue determined by the investigator, then the quantity of ozone to be introduced into the water will be (in the case where the amount of residue is kept constant in the industrial reactor):

$$D + r + r\ at = D + r\ (1 + at)$$

The treatment dose will depend on the loss of ozone entrained by the ozonized air leaving the reactor. It depends essentially on the form of the reactor, the time of contact of the ozonized air and the water, and the ozone residue. This is why it is highly desirable to conduct the laboratory experiments with a residue similar to that applied in practice. The loss p can be estimated to be in the region of 10 to 30%, and under these conditions:

$$\frac{D + r\ (1 + at)}{0.9} < T < \frac{D + r\ (1 + at)}{0.7}$$

REMARKS

1) In the method of measurement described above the residue value does not remain constant but decreases from its initial value:

$$r_o = re^{at}$$

where r is the residue measured at time t.

The same situation arises in industrial reactors with a single point injection. If r is the residue required at the outlet, after a contact-time t, the quantity of ozone consumed by the water will be:

$$D + r_o - r = D + r\ (e^{at} - 1)$$

and the treatment dose will be

$$\frac{D + r\ (e^{at} - 1)}{0,9} < T < \frac{D + r\ (e \quad - 1)}{0,7}$$

this value always being greater than that in reactors where the residue r has a constant value.

2) The appendix contains a brief account of the procedure used for virulicidal treatment requiring an ozone residue of 0.4 mg/l for a reaction time of $\geq$ 4 min.

APPENDIX

DETERMINATION OF THE CHARACTERISTICS OF WATER IN RELATION TO OZONE AND OF THE INDUSTRIAL OZONIZATION DOSE

1. PRINCIPLE

The aim of the operation is to determine:

- the instantaneous chemical ozone demand;
- the specific auto-decomposition coefficient;
- the industrial ozonization dose.

To this end a known quantity of ozonized air is brought into intimate contact with a fixed volume of the water under examination, and the residual ozone dissolved in this water after contact times of 1 min and 4 min is measured.

2. DESCRIPTION OF THE EQUIPMENT USED

2.1. TRAILIGAZ LABO 66 laboratory ozonization unit

2.2. Volumetric flask

The ozonization reaction takes place in a 600 ml volumetric flask with a graduation at 500 ml.

A ground-glass stopper fitted with a tap enables the flask to be completely filled with the water being examined.

A side tap, placed on the neck of the flask below the 500 ml mark, enables the contents of the flask to be drained off down to 500 ml.

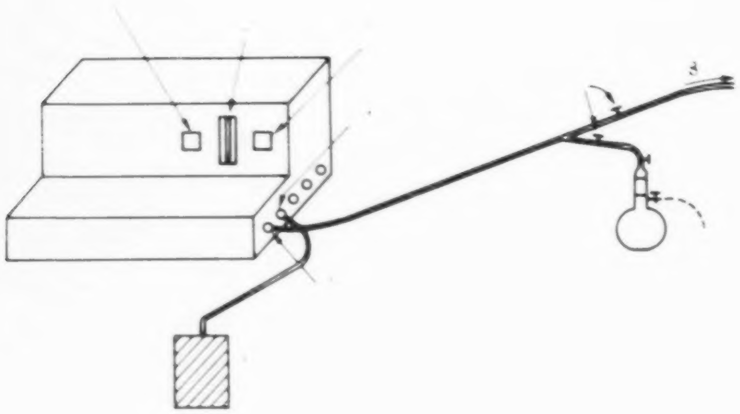


Fig. 1 Ozonization unit

1 = wattmeter; 2 = flow-meter; 3 = manometer;
4 = dry air inlet; 5 = sampling valve;
6 = compressor; 7 = Mohr clip; 8 = free air

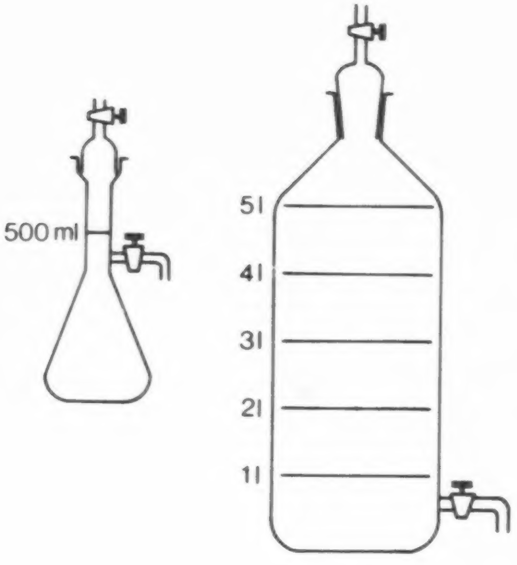


Fig. 2

Measurement of the ozone demand; special flasks

3. PROCEDURE

3.1. Method of obtaining the ozonized air

- Determine flow rate and the power consumption*.
- Start the cooling water circulation of the ozonization unit.
- Start the air compressor.
- Regulate the air flow rate by means of the sampling valve (the flow rate valve being closed). The delivery-rate is read off a flow-meter (reading at the top of the ball).
- Regulate the air pressure by means of the pressure valve; the pressure should be set at 0.5 kg/cm^2 (the calibration curves of the ozonization unit were plotted for this pressure).
- Apply power to the ozonization unit.

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* The concentration of ozone in the ozonized air produced depends on two parameters: the air flow rate and the power consumption. The calibration curves of the ozonization unit enable a flow rate and a power consumption corresponding to the desired concentration of ozone to be determined. The choice of the latter depends on the nature of the water being studied, the aim being to obtain a residue of 0.4 mg of ozone per litre of water after a water-ozone contact time of 4 min (see Section 3.2). In cases where this residue is below a value of 0.3, or above a value of 0.6, it is necessary to repeat the experiment with a higher or lower ozone concentration of the air. In the case where the highest possible concentration of the ozonized air does not give a residue of 0.3, a special 6 litre flask must be used, which enables the air/water volume ratio to be varied from 1/5 to 5/1, this ratio being first made 1/2 and then higher if necessary. By way of an indication, a content of 10 mg of ozone per litre of air is suitable for only slightly polluted water (such as well water).

- Turn the power handwheel clockwise to obtain the desired power consumption; this is read off the wattmeter.
- Wait for five minutes to achieve stable flow rate and power consumption.

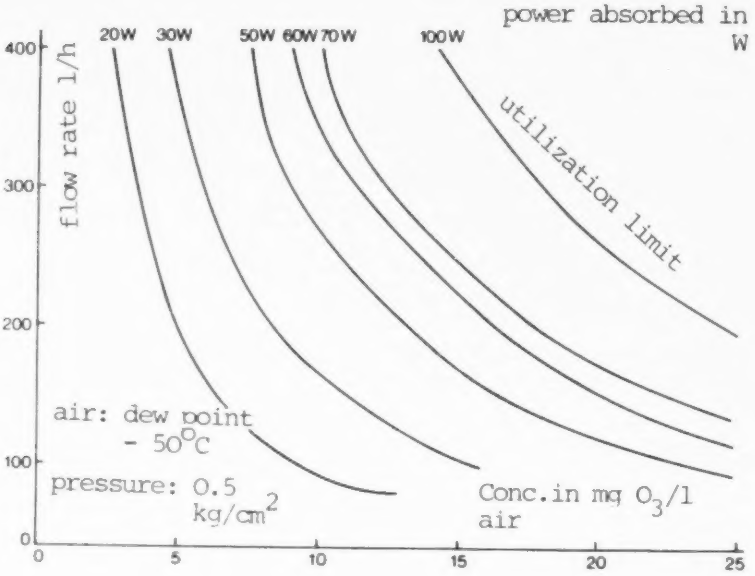


Fig. 3 Mean air production curves for the LABO 66 unit

3.2. Performance of the ozonization

- Fill the flask described in Section 1.2 with the water to be ozonized.
- Connect the ozonized air pipe branched to the sampling valve to the upper arm of the ground-glass stopper; the end can be partially closed by means of a Mohr clip opening to the atmosphere.

- When the Mohr clip has been adjusted so as to produce a steady flow of ozonized air to the atmosphere during the following operation, open the side tap of the flask so that the water level descends to the 500 ml mark. The gas volume on top is now occupied by ozonized air at a concentration corresponding to the ozonizer setting.

- Close the tap on the ground-glass stopper and disconnect the ozonized air inflow.

- Shake the flask vigorously for 20 sec, timing this with a stopwatch. (The ozonization reaction and the establishment of an ozone equilibrium between the air and the water take place during these 20 sec).

- Let the flask stand for 2 min, then tilt it so that the water clears the side outlet; the remaining ozonized air is expelled by blowing air into the end of this outlet. Determine the residual ozone in the water as described below.

- Repeat the experiment, this time letting the flask stand for 4 min instead of 2 min.

- Repeat as above, this time letting the flask stand for 8 min.

3.3. Determination of the residual ozone

- Immediately after this time (2, 4, or 8 min), place several crystals of potassium iodide in the flask. The residual ozone oxidizes the iodide to iodine. Pour the 500 ml of the iodine solution into a conical flask, and 2 ml of 1:2 H_2SO_4, and titrate with sodium thiosulphate.

Refer to the method of determination of residual ozone in the water.

4. CALCULATION

4.1. Determination of the auto-decomposition coefficient (-a)

Find the mean of the three values obtained with the aid of the equations below* :

$$-a\ (\min^{-1}) = \frac{1}{2}\ \ln \frac{r_4}{r_2} = \frac{1}{4}\ \ln \frac{r_8}{r_2} = \frac{1}{6}\ \ln \frac{r_8}{r_2}$$

where r_2, r_4, and r_8 are the residual amounts of ozone after contact times of 2, 4, and 8 min respectively.

4.2. Determination of the immediate ozone demand (D)

By definition, the immediate ozone demand is:

$$D = C_o - r_o$$

where C_o is the initial ozone concentration in water, introduced by means of the air-water contact; it is calculated as in Section 4.21,

and r_o is the residual concentration of ozone in the water at time 0, calculated as in Section 4.22.

4.21. Calculation of C_o

$$C_o = \frac{cv}{\left(\frac{v}{s}\right) + V}$$

where v is the volume of ozonized air in contact with the water

V is the volume of water in contact with V_1,

---

* If r_8 is less than 0.2, the following value will be retained:

$$a = \frac{1}{2}\ \ln \frac{r_4}{r_2}$$

c is the concentration of ozone in the ozonized air,

S is the distribution coefficient of the ozone between the water and the air; the value of this coefficient, which is a function of the temperature, is determined with the aid of Fig. 4 in the Appendix.

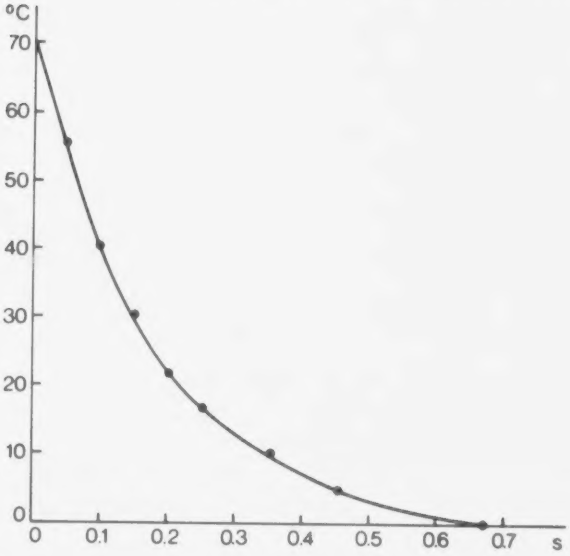


Fig. 4

Henry's coefficient (S) as a function of temperature θ
$S = f(\theta)$

4.22. Calculation of r_o

r_o is found from the equations below (take the mean of the 3 values otbained, or of the first two if r_8 is less than 0.2):

$$\ln \frac{r_o}{r_2} = 2a$$

$$\ln \frac{r_o}{r_4} = 4a$$

$$\ln \frac{r_o}{r_8} = 8a$$

where a is the auto-decomposition coefficient calculated in Section 4.1 and r_2, r_4, and r_8 are the residues of ozone after respective ozone-water contact times of 2, 4, and 8 min.

OZONE INPUT

W.J. Masschelein

As far as the mode of action and the passage of ozone into water are concerned, at least two essentially different mechanisms must be taken into consideration:

1) contact with bubbles of strongly ozonized air; we were able to show (cf. our report to the Berliner Wasser-congress in 1976) that as regards the bactericidal action of ozone this mechanism plays a very important if not the main part. Similarly, the literature data on the use of ozone in the preliminary treatment of water can be interpreted as favouring micelle formation. This mode of action is illustrated by the rapid bactericidal action obtained during the passage of the ozone from the gaseous into the dissolved phase.

2) continuous, stepwise, and slow action of the residual dissolved ozone; this mechanism is particularly suitable for combatting impurities more resistant to oxidation, for example detergents. This mode of action corresponds to first-order kinetics with respect to the concentration of the dissolved ozone and also seems to be of decisive importance for the viricidal action.

Therefore,during the planning and layout of an ozonization plant these two basically different action mechanisms must be borne in mind: passage of the ozone must be ensured, e.g. with the aid of turbines, and a relatively short contact time (less than 1 min) is necessary; the effect is thus achieved by the contact with bubbles of strongly ozonized air. On the other hand, the slow mode of action of the residual ozone in the after-treatment requires a time of at least 6 min. During this period a concentration of 0.2 to 0.4 g O_3/m^3 must be maintained.

OZONIZATION BY-PRODUCTS AND THEIR REMOVAL BY COAGULATION

J.C. Kruithof

1. Introduction

In surface water, taking the river Rhine as an example, many organic micro-pollutants may be found. One of the most important groups of pollutants is the fraction of the aromatics (1-3). In this fraction many alkylated, hydroxylated, chlorinated and nitrated mono-aromatics and poly-aromatics can be present. These impurities must be removed in the process of drinking water treatment. One of the processes to remove these compounds is ozonization. In this paper the ozonization of phenol, naphthalene and phenanthrene will be discussed. In particular, the production and stability of organic peroxides will be mentioned. Furthermore, the formation of dialdehydes and their conversion to carboxylic acids will be discussed. The ozonizations have been carried out at a pH of about 7, so the initial reaction of ozone will be an electrophilic substitution and not a reaction of ozone with hydroxylic ions.

In the second part of the paper some examples are given for the removal of carboxylic acids produced during ozonization by coagulation with aluminium salts. The removal of oxalic acid, o-phthalic acid and 1,3,5-benzene tricarboxylic acid will be reported. The models for removal are based on the hydrolysis of the metal salt used, the dissociation of the carboxylic acid, the complexing of the metal ion with the carboxylate ion and the solubility of the metal hydroxide used.

2. Ozonization of some aromatic compounds

2.1 Ozonization of phenol

Many authors describe the ozonization of phenol in water. Bauch et al. (4) assume the formation of an ozonide which is converted to smaller molecules, and a direct oxidation by which the benzene ring is ruptured. Eisenhauer (5-7) finds catechol and o-benzo quinone as the first reaction products. Gould (8, 9) states three mechanisms: hydroxylation, cleavage of the benzene ring and the production of polymeric compounds. According to our own investigations, two major reaction paths occur, the first of which, taking place for about 30 %, is hydroxylation producing catechol and hydroquinone as reaction products. The concentration of these products is given in Figure 1. Both concentrations reach a maximum after an ozone consumption of $3.6 \cdot 10^{-3}$ moles (0.4 moles of ozone/mole of phenol originally present).

In addition, there is a rupture of the benzene ring for 70 %, producing an aldehydic and an acid hydroperoxide. Both peroxides prove to be unstable and will either cause an elimination of H_2O_2 or rearrangement. An elimination of H_2O_2 will convert the aldehydic peroxide to glyoxal. When a rearrangement takes place the aldehydic peroxide is converted into two moles of formic acid, the acid peroxide rearranges to one mole of formic acid and one mole of CO_2. The concentration of glyoxal and H_2O_2 is given in Fig. 2, and that of formic acid and CO_2 in Fig. 3. The concentrations of glyoxal, H_2O_2 and formic acid reach a maximum after an ozone consumption of about $26 \cdot 10^{-3}$ moles (2.9 moles of ozone/mole of phenol).

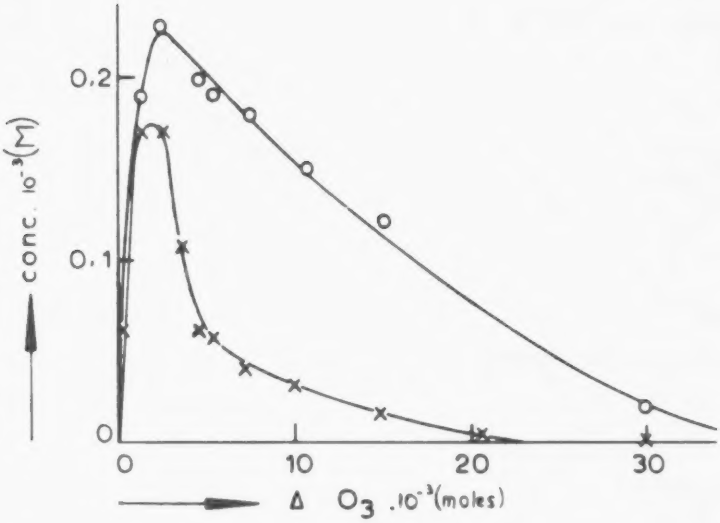


Fig. 1 The concentration of catechol and hydroquinone as a function of the ozone-uptake (x = catechol; o = hydroquinone)

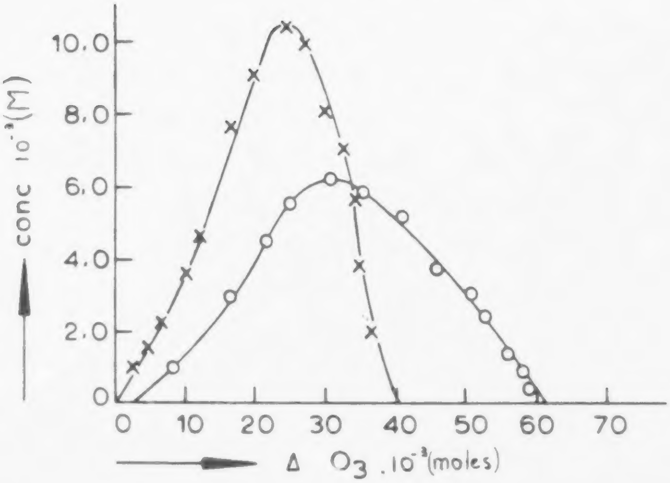


Fig. 2 The concentration of glyocal and H_2O_2 as a function of the ozone-uptake (x = glyoxal; o = H_2O_2)

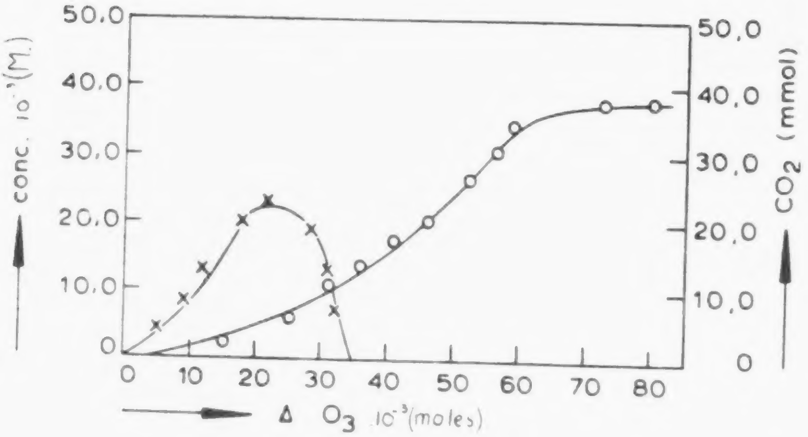


Fig. 3 The concentration of formic acid and the CO_2-production as a function of the ozone-uptake (x = formic acid; o = carbon dioxide)

At this point all phenol has reacted with ozone. In consecutive reactions glyoxal is converted to glyoxylic acid, forming oxalic acid. In the absence of H_2O_2 oxalic acid proves to be a stable final product. Formic acid is oxidized to CO_2. The concentration of the organic compounds formed by secondary reactions is presented in Fig. 4. At the end of the reaction, at an ozone consumption of $70 \cdot 10^{-3}$ moles, 75 % of all carbon atoms are found as CO_2 and 25 % in the form of oxalic acid.

It can therefore be concluded that when ozonizing phenol, 30 % will be hydroxylated to catechol and hydroquinone, while 70 % of the phenol will produce unstable peroxides which eliminate H_2O_2 or rearrange to glyoxal, formic acid, or CO_2. CO_2 and oxalic acid are the only final products. The complete ozonization of phenol is shown in scheme 1.

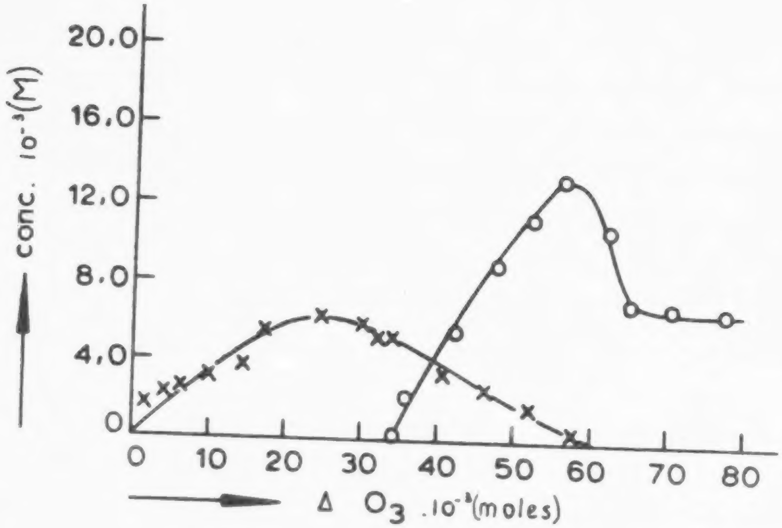
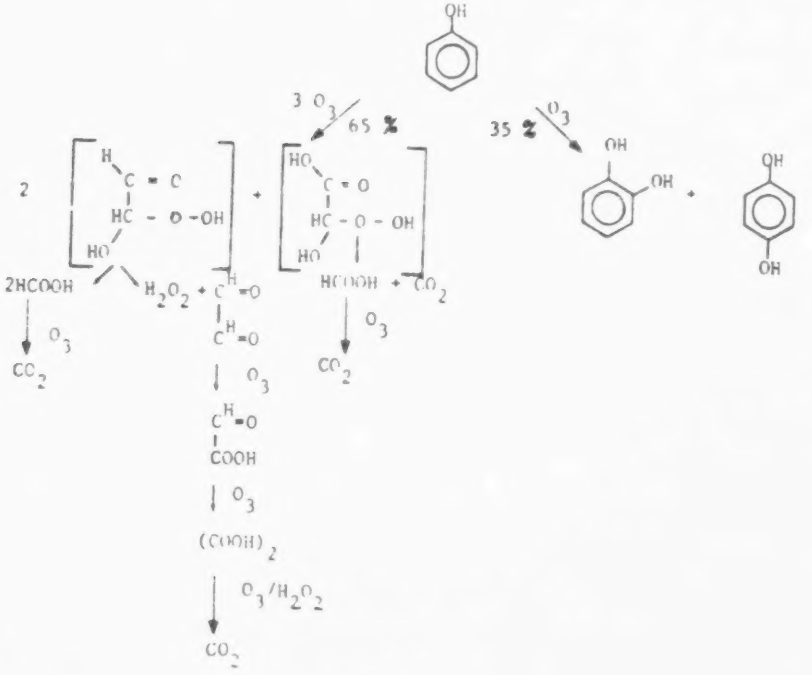


Fig. 4 The concentration of glyoxylic acid and oxalic acid as a function of the ozone-uptake (x = glyoxylic acid; o = oxalic acid)



Scheme 1 The ozonization of phenol

2.2 The ozonization of naphthalene

Many authors describe the ozonization of naphthalene in organic solvents. Bailey et al. (10-12) ozonize naphthalene in CCl_4 and methanol. They assume that there is production of a mono-ozonide in CCl_4, while in methanol they identify two cyclic aromatic peroxides, which prove to be rather stable. Sturrock et al. (13) ozonize naphthalene in mixtures of water and acetone. They assume an equilibrium between an open and a cyclic peroxide.

From our own experiments we can conclude that an open hydroxy-hydroperoxide is produced after an ozone consumption of 2 moles/mole of naphthalene originally present. This open peroxide proves to be unstable and results in a cyclization or an elimination of H_2O_2. In the first case a cyclic peroxide (a 1,2-dioxane derivative) is formed.

The concentration of this compound is presented in Fig. 5. It can be seen that the concentration of the cyclic peroxide reaches a maximum after an ozone consumption of $16 \cdot 10^{-3}$ moles (2.9 moles of ozone/mole of naphthalene). The highest concentration found is $2.3 \cdot 10^{-3}$ M, indicating that about 45 % of the total naphthalene originally present will produce this peroxide. For the remaining 55 % an elimination of H_2O_2 takes place, forming o-phthalaldehyde as the organic product. Both concentrations are shown in Fig. 6. Again, the concentrations reach a maximum after an ozone consumption of $16 \cdot 10^{-3}$ moles. The highest concentrations found are $2.8 \cdot 10^{-3}$ M and $2.7 \cdot 10^{-3}$ M for o-phthalaldehyde and H_2O_2, respectively. Without an additional ozone supply all aromatic compounds are converted to o-phthalic acid. The concentration of this compound is shown in Fig. 7. It can be seen that after an ozone consumption of $32 \cdot 10^{-3}$ moles (5.4 moles/mole of naphthalene originally present) the concentration of o-phthalic acid is $6.5 \cdot 10^{-3}$ M. This means that about 90 % of all naphthalene originally present are converted to o-phthalic acid, which proves to be rather stable against further ozonization. After an extensive ozonization, 70 % of all carbon atoms are measured as CO_2 and 30 % as oxalic acid.

Therefore, when naphthalene reacts with ozone, an open peroxide is produced. 45 % of this peroxide are converted to a very stable cyclic peroxide, 55 % result in an elimination of H_2O_2, yielding o-phthalaldehyde. Both organic compounds form o-phthalic acid with an additional supply of ozone. The first part of ozonization of naphthalene is illustrated in scheme 2.

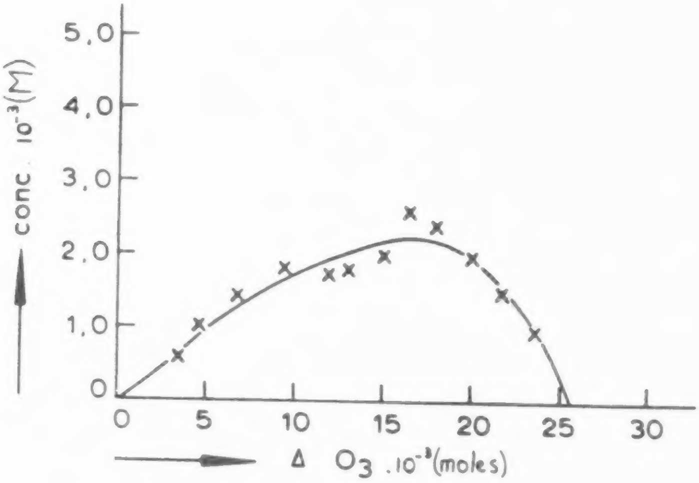


Fig. 5 The concentration of 3,6-dihydroxy-4,5-benzo-1,2-dioxane as a function of the ozone-uptake

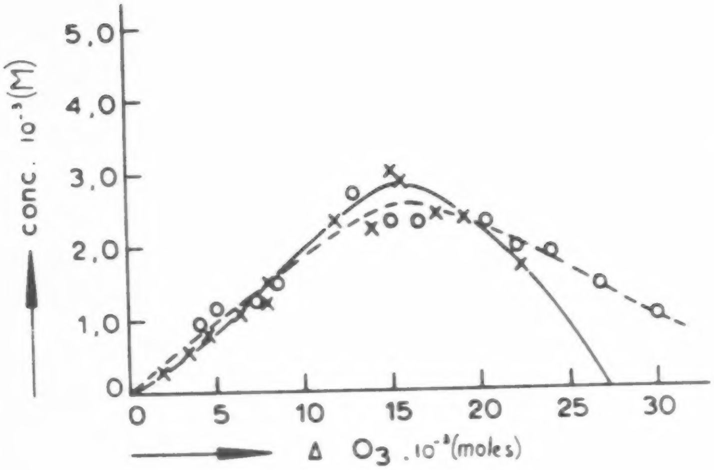


Fig. 6 The concentration of o-phthalaldehyde and H_2O_2 as a function of the ozone-uptake
(x = o-phthalaldehyde; o = H_2O_2)

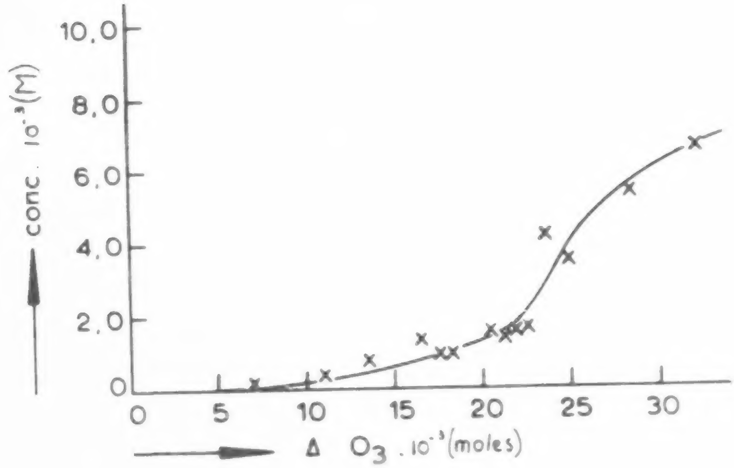
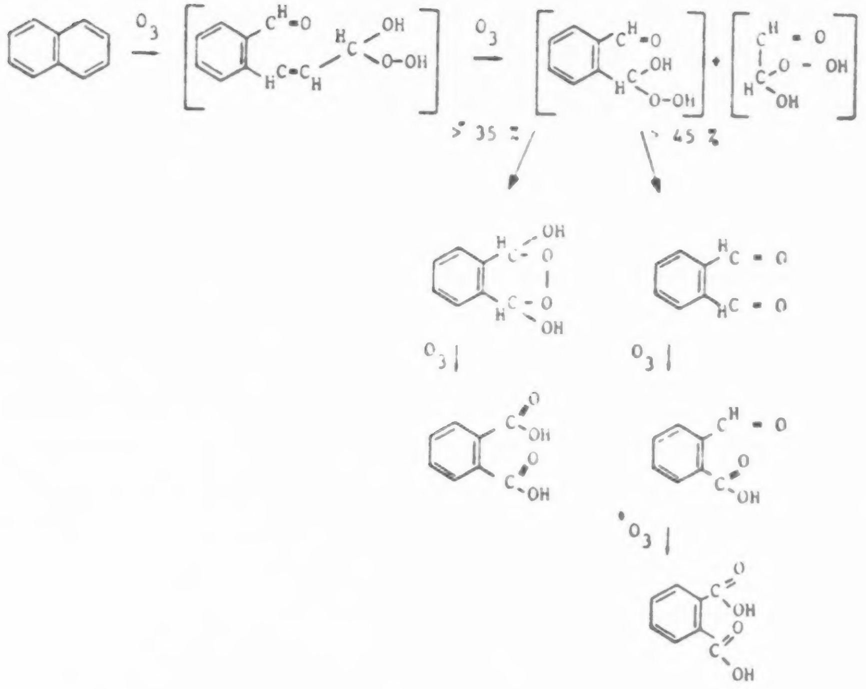


Fig. 7 The concentration of o-phthalic acid as a function of the ozone-uptake



Scheme 2 The first phase of the ozonization of naphthalene

2.3 The ozonization of phenanthrene

As for naphthalene, several authors describe the ozonization of phenanthrene in organic solvents. Schmitt et al. (14) ozonize phenanthrene in chloroform and find an iso ozonide. Bailey et al. (15, 16) ozonize phenanthrene in methanol and identify a cyclic peroxide. The same mechanism is given by Sturrock et al. (17) for the ozonization of phenanthrene in water-alcohol mixtures.

Our own experiments indicate the production of an open hydroxy-hydroperoxide after an ozone consumption of $5 \cdot 10^{-3}$ moles of ozone (1 mole/mole of phenanthrene originally present). In this case the open peroxide cyclizizes for less than 5 %, and an almost complete elimination of H_2O_2 takes place, forming 2,2'-diphenaldehyde as the organic product. Both concentrations are given in Fig. 8. In this Figure, a maximum concentration is shown for diphenaldehyde of $3.6 \cdot 10^{-3}$ at an ozone consumption of $5.0 \cdot 10^{-3}$ moles. An additional ozone supply produces a conversion to diphenic acid which proves to be fairly stable against ozonization. After an extensive ozonization, CO_2 and oxalic acid are the only final products.

Thus an open peroxide is produced when ozonizing phenanthrene. This peroxide is almost completely converted to 2,2'-diphenaldehyde and H_2O_2. The aldehyde produces diphenic acid when reacting with ozone. The first part of the ozonization of phenanthrene is shown in scheme 3.

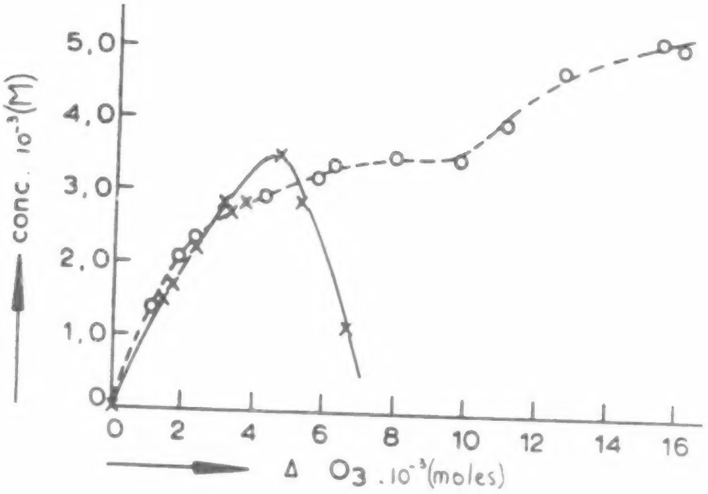
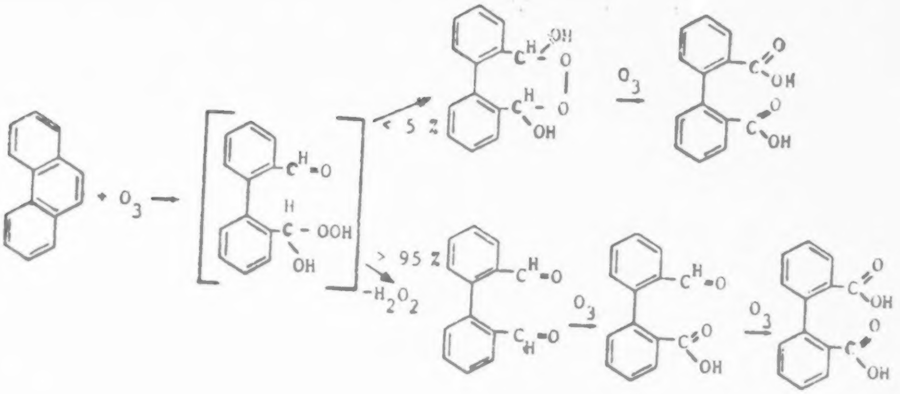


Fig. 8 The concentration of diphenaldehyde and H_2O_2 as a function of the ozone-uptake
(x = diphenaldehyde; o = H_2O_2)



Scheme 3 The first phase of the ozonization of phenanthrene

2.4 Conclusions from the ozonization experiments and discussion

From the above described and additional experiments (1) the following conclusions can be **drawn**:

1. When ozonizing aromatic compounds H_2O_2 is always produced. H_2O_2 will be removed by exhaustive ozonization.

2. When ozonizing poly-aromatics, very stable organic peroxides can be formed if the initial attack of ozone produces an aldehyde group and a hydroxy-hydroperoxide group in ortho position at the same benzene ring.

3. In all other cases when ozonizing poly-aromatics dialdehydes and H_2O_2 are produced almost completely.

4. The organic peroxides as well as the dialdehydes are converted into carboxylic acids such as o-phthalic acid, diphenic acid, oxalic acid, etc., with an additional supply of ozone. When ozonizing larger organic

molecules (such as humic acid), benzene polycarboxylic acids (such as 1,3,5-benzene tricarboxylic acids) are produced. These acids are rather stable against further ozonization.

5. Formic acid, glyoxalic acid and oxalic acid are the only aliphatic acids formed when ozonizing phenol, naphthalene and phenanthrene. Oxalic acid proves to be a stable end-product in the absence of H_2O_2.

Exhaustive ozonization can never be carried out economically, so that many carboxylic acids can be present in the ozonated effluent. These compounds must be removed in a subsequent purification step such as activated carbon filtration or a secondary coagulation step. The second part of the paper gives some theoretical and experimental results for the secondary coagulation step.

3. Removal of carboxylic acids with aluminium salts

In this part of the paper some models will be presented by which the removal of carboxylic acids produced by ozonization can be described. For a quantitative approach the following constants must be known:

- Stability constants for the hydrolysis of the metal salt used (${}^{*}\beta_1$-${}^{*}\beta_4$).
- Dissociation constants for the carboxylic acid (K_1-K_n).
- Stability constants of the produced metal carboxylate complexes (β_1-β_n), and in case of soluble complexes:
- The solubility product of the metal hydroxyde (${}^{*}K_{SO}$).

Based on differences in these properties, the following mechanisms of removal may occur:

1. Formation of a soluble, strong, negative complex. The removal of this complex takes place by adsorption of the complex on a floc of metal hydroxyde. The pH is a function of the metal salt concentration and varies between the pH for optimum complexation and the iso-electrical point.
2. Formation of a soluble, weak complex. The removal is caused by adsorption of free carboxylate ions on a floc of metal hydroxyde. The optimum pH coincides with the iso-electrical point.
3. Formation of an insoluble complex, which is removed as such. The optimum pH coincides with the pH for optimum complexation.

With all carboxylic acids and with aluminium salts,as well as with ferric salts, the same calculations can be used. In this paper the complete calculation will only be given for the removal of oxalic acid with aluminium salts. The experimental part will describe the removal of oxalic acid as well as the removal of o-phthalic acid and 1,3,5-benzene tricarboxylic acid.

3.1 The hydrolysis of aluminium salts

Aluminium ions are hydrated in strong acid solutions with 6 coordinatively bound water molecules. When the pH rises the following steps of hydrolysis take place:

$$\mathrm{Al\,(H_2O)_6}^{3+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Al(H_2O)_5OH}]^{2+} + \mathrm{H_3O^+}$$

$$[Al(H_2O)_5OH]^{2+} + H_2O \rightleftharpoons [Al(H_2O)_4(OH)_2]^{+} + H_3O^{+}$$

$$[Al(H_2O_4(OH)_2]^{+} + H_2O \rightleftharpoons [Al(H_2O)_3(OH)_3] + H_3O^{+}$$

$$[Al(H_2O)_3(OH)_3] + H_2O \rightleftharpoons [Al(H_2O)_2(OH)_4]^{-} + H_3O^{+}$$

According to Sillèn and Martell (18,19) these reactions have the following stability constants :

$${}^{*}\beta_1 = 10^{-4,89}; \quad {}^{*}\beta_2 = 10^{-9,37}; \quad {}^{*}\beta_3 = 10^{-15,04}; \quad {}^{*}\beta_4 = 10^{-20,30}$$

According to Schwarzenbach (20) an $\alpha_{Al(OH)}$ can be defined. This $\alpha_{Al(OH)}$ gives the ratio of the sum of the concentrations of all metal ions over the concentration of Al^{3+} :

$$\alpha_{Al(OH)} = \frac{[Al']}{[Al^{3+}]} = \frac{[Al^{3+}]+[Al(OH)^{2+}]+[Al(OH)_2{}^{+}]+[Al(OH)_3]+[Al(OH)_4{}^{-}]}{[Al^{3+}]} \qquad (1)$$

This formula is valid when no polynuclear complexes are produced. This can be assumed as will be shown in a following paper (21). Introducing the stability constants gives :

$$\alpha_{\ Al(OH)} = 1 + \frac{10^{-4,89}}{[H^+]} + \frac{10^{-9,37}}{[H^+]^2} + \frac{10^{-15,04}}{[H^+]^3} + \frac{10^{-20,30}}{[H^+]^4} \qquad (2)$$

The log $\alpha_{Al(OH)}$ as a function of the pH is given in Figure 9.

3.2 The dissociation of oxalic acid

Oxalic acid dissociates in two steps (22)

$$H_2Ox + H_2O \rightleftharpoons HOx^- + H_3O^+ \qquad K_1 = \frac{[HOx^-][H_3O^+]}{[H_2Ox]} = 5{,}9 \times 10^{-2} \qquad (3)$$

$$HOx^- + H_2O \rightleftharpoons Ox^{2-} + H_3O^+ \qquad K_2 = \frac{[Ox^{2-}][H_3O^+]}{[HOx^-]} = 6{,}4 \times 10^{-5} \qquad (4)$$

As with the hydrolysis of aluminium salts an $\alpha_{Ox(H)}$ can be defined

$$\alpha_{Ox(H)} = \frac{[Ox']}{[Ox^{2-}]} = \frac{[H_2Ox] + [HOx^-] + [Ox^{2-}]}{[Ox^{2-}]} \qquad (5)$$

Introducing the dissociation constants of oxalic acid gives

$$\alpha_{Ox(H)} = 1 + \frac{[H_3O^+]}{K_2} + \frac{[H_3O^+]^2}{K_1K_2} \qquad (6)$$

Log $\alpha_{Ox(H)}$ calculated with formula (6) is reprensented in Figure 10.

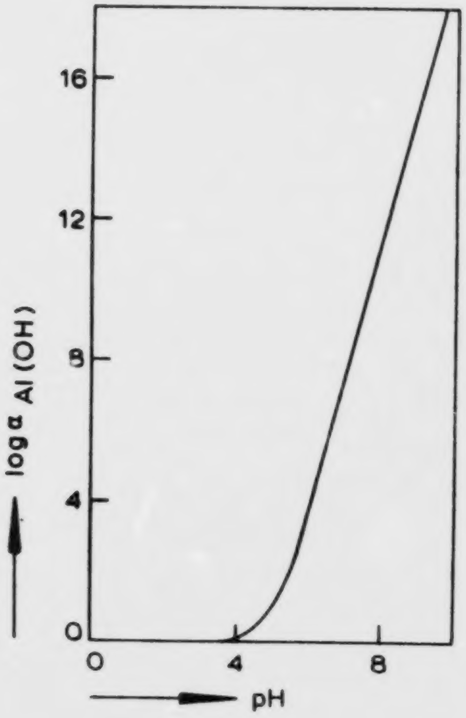


Fig. 9
Log $\alpha'_{Al(OH)}$ as a function of the pH

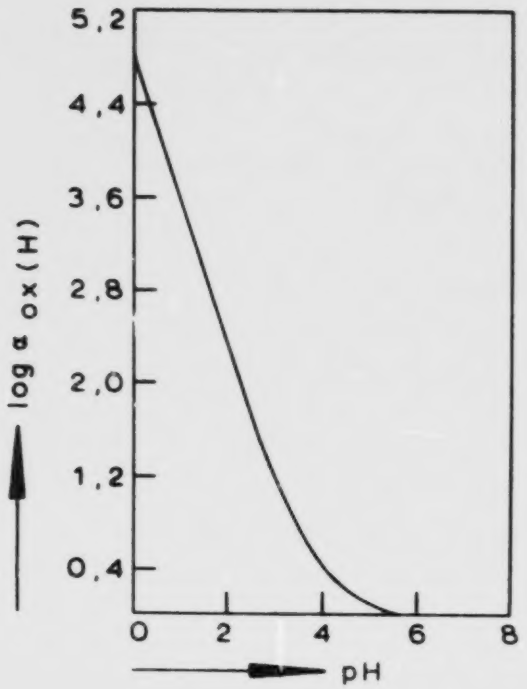


Fig. 10
Log $\alpha_{Ox(H)}$ as a function of the pH

3.3 The complexation of the aluminium-ion with oxalate-ions

The aluminium-ion forms, with oxalate-ions, the following complexes (1,23) :

$$Al^{3+} + Ox^{2-} \rightleftharpoons Al(Ox)^{+} \quad \beta_1 = \frac{[Al(Ox)^{+}]}{[Al^{3+}][Ox^{2-}]} = 10^{7,26} \qquad (7)$$

$$Al^{3+} + Ox^{2-} \rightleftharpoons Al(Ox)_2^{-} \quad \beta_2 = \frac{[Al(Ox)_2^{-}]}{[Al^{3+}][Ox^{2-}]^2} = 10^{13,0} \qquad (8)$$

$$Al^{3+} + 3Ox^{2-} \rightleftharpoons Al(Ox)_3^{3-} \quad \beta_3 = \frac{[Al(Ox)_3^{3-}]}{[Al^{3+}][Ox^{2-}]^3} = 10^{16,8} \qquad (9)$$

For this complexation the following $\alpha_{Al(Ox)}$ can be defined :

$$\alpha_{Al(Ox)} = \frac{[Al']}{[Al^{3+}]} = \frac{[Al^{3+}] + [Al(Ox)^{+}] + [Al(Ox)_2^{-}] + [Al(Ox)_3^{3-}]}{[Al^{3+}]} \qquad (10)$$

Introducing the stability constants β in formula (10) gives :

$$\alpha_{Al(Ox)} = 1 + \beta_1[Ox^{2-}] + \beta_2[Ox^{2-}]^2 + \beta_3[Ox^{2-}]^3 \quad (11)$$

With the help of formula (5), formula (11) can be written as :

$$\alpha_{Al(Ox)} = 1 + \frac{\beta_1[Ox']}{\alpha_{Ox(H)}} + \frac{\beta_2[Ox']^2}{\alpha^2_{Ox(H)}} + \frac{\beta_3[Ox']^3}{\alpha^3_{Ox(H)}} \quad (12)$$

So $\alpha_{Al(Ox)}$ can be calculated as a function of the pH when the oxalic acid concentration is known. The $\alpha_{Al(Ox)}$ for oxalic acid concentrations of 10^{-3}, 10^{-4} and 10^{-5} M is given in Figure 11.

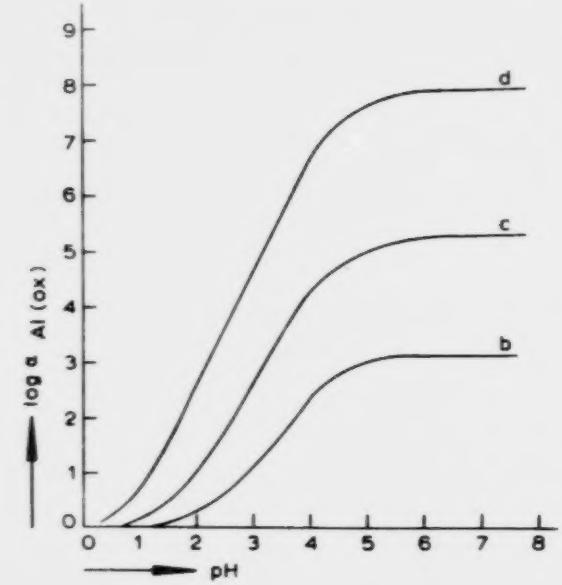


Fig. 11 Log $\alpha_{Al(Ox)}$ as a function of the pH for three oxalate concentrations;
b: $[Ox'] = 10^{-5}$M; c: $[Ox'] = 10^{-4}$M; d: $[Ox'] = 10^{-3}$M

Besides an α_{Al}^{tot} can be defined covering all aluminium compounds :

$$\alpha_{Al}^{tot} = \frac{[Al']}{[Al^{3+}]} = \frac{[Al^{3+}] + \sum[Al(Ox)_m] + \sum[Al(OH)_n]}{[Al^{3+}]} \qquad (13)$$

With formula (1) and (10) formula (13) can be converted to :

$$\alpha_{Al}^{tot} = \alpha_{Al(Ox)} + \alpha_{Al(OH)} - 1 \qquad (14)$$

$\alpha_{Al(Ox)}$ and $\alpha_{Al(OH)}$ are known by now, so α_{Al}^{tot} can be calculated.

To describe the removal of oxalic acid with aluminium salts it is important to know the pH-range where the concentration of aluminium oxalate complexes dominates over all other concentrations. Therefore an $\alpha'_{Al(Ox)}$ can be defined:

$$\alpha'_{Al(Ox)} = \frac{[Al^{3+}] + \sum[Al(Ox)_m] + \sum[Al(OH)_n]}{[Al^{3+}] + \sum[Al(OH)_n]} \qquad (15)$$

With formula (1) and (10) formula (15) can be converted to :

$$\alpha'_{Al(Ox)} = \frac{\alpha_{Al(OH)} + \alpha_{Al(Ox)} - 1}{\alpha_{Al(OH)}} = \frac{\alpha_{Al}^{tot}}{\alpha_{Al(OH)}} \qquad (16)$$

or

$$\log \alpha'_{Al(Ox)} = \log \alpha_{Al}^{tot} - \log \alpha_{Al(OH)} \qquad (17)$$

Log $\alpha_{Al(Ox)}$ can be calculated as a function of the pH when the total concentration of oxalic acid is known. For oxalic acid concentrations of 10^{-3}, 10^{-4} and 10^{-5} M log $\alpha'_{Al(Ox)}$ is represented in Figure 12.

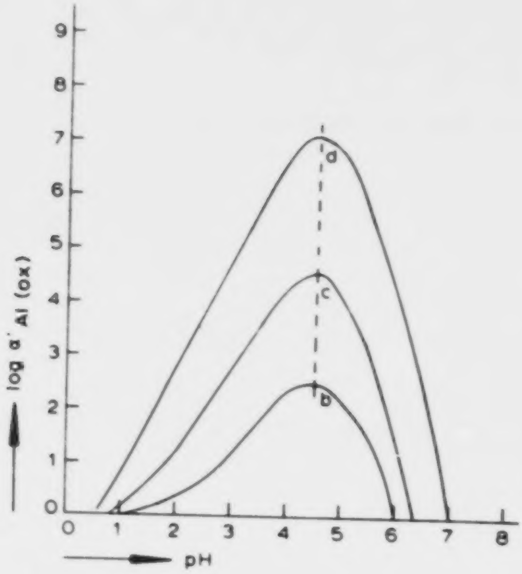


Fig. 12 Log $\alpha'_{Al(Ox)}$ as a function of the pH for three oxalate concentrations;
b: $[Ox'] = 10^{-5}$M; c: $[Ox'] = 10^{-4}$M; d: $[Ox'] = 10^{-3}$M

3.4 The precipitation of aluminium hydroxide

When the produced complexes between aluminium and the carboxylic acids are soluble in water, as is the case with oxalic acid, the precipitation of aluminium hydroxyde plays an important part. The precipitation of the hydroxyde can be represented by the following simple reaction :

$$Al^{3+} + 3\ OH^- \rightleftharpoons Al(OH)_{3,\ S}$$

For this reaction the following dissociation constant is known (18) :

$$K_{SO} = [Al^{3+}][OH^-]^3 = 10^{-34} \quad \text{or} \quad {}^{*}K_{SO} = \frac{[Al^{3+}]}{[H_3O^+]^3} = 10^8 \qquad (18)$$

Together with formula (13) this can be written as

$$^{*}K_{SO} = \frac{[Al']}{[H_3O^+]^3\,\alpha_{Al}^{tot}} = 10^8 \qquad (19)$$

Formula (19) gives the limiting aluminium concentration for hydroxyde precipitation as a function of the pH and the oxalic acid concentration. The results are represented in Figure 13.

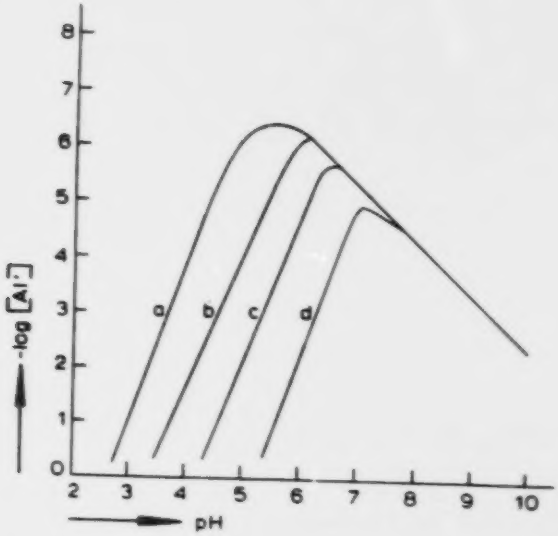


Fig. 13 Log [Al'] for minimum hydroxyde precipitation as a function of the pH with the following oxalate concentrations;

a: [Ox'] = 0 M; b: [Ox'] = 10^{-5} M; c: [Ox'] = 10^{-4};
d: [Ox'] = 10^{-3}M

3.5 Discussion and presentation of the mechanisms for removal

From paragraphs 3.1 to 3.4 and from Figs. 9 to 13 the following conclusions can be drawn:

- At a pH higher than 4 aluminium salts hydrolyse to aluminium hydroxyl complexes.
- At a pH higher than 5.5 oxalic acid is completely dissociated into oxalate ions.
- Independent of the concentration of oxalic acid $\alpha'_{Al(Ox)}$ reaches a maximum at a pH of about 4.5. So at a pH of 4.5 the complexation dominates over the hydrolysis as much as possible. The value of $\alpha'_{Al(Ox)}$ varies between 2.5 and 7.1 indicating that aluminium ions produce strong complexes with oxalate ions.
- The minimum aluminium concentration for precipitation of $Al(OH)_3$ is a function of the concentration of oxalic acid.
- Besides, it is known that aluminium oxalate complexes are soluble in water.

From these facts it can be concluded that oxalic acid is removed via mechanism 1. It forms soluble, negatively charged strong complexes at an optimum pH of 4.5. At this pH optimum removal takes place when enough aluminium hydroxyde is precipitated. At low concentrations of aluminium this will not be the case, so the optimum pH for removal will shift to higher values.

Based on the same kind of calculations it can be concluded that o-phthalic acid is removed by way of mechanism 2. It gives very weak complexes, which are soluble in water. The removal takes place by adsorption of free phthalate-ions on a floc of $Al(OH)_3$. 1,3,5-benzene tricarboxylic acid is removed via mechanism 3. It forms rather weak complexes, which are insoluble in water. The removal will take place by precipitation of the complex.

The proposed mechanisms for removal will be tested in the experimental part.

3.6 Experiments

To check the proposed mechanisms for removal, experiments have been carried out with a constant concentration of carboxylic acid of about 10^{-4} M and a varying pH and aluminium dose. The results for oxalic acid are presented in Fig. 14. From this figure it can be concluded that the optimum pH for the oxalic acid removal is a function of the aluminium-salt concentration. At an aluminium-salt concentration of 10^{-4} M the optimum pH is 6.8. This pH coincides with the iso-electrical point of $Al(OH)_3$. At higher aluminium-salt concentrations the optimum pH drops to lower values, approaching the pH where $\alpha_{Al(Ox)}$ reaches its maximum. At very high concentrations of aluminium (5×10^{-3} M) the oxalic acid removal reaches a maximum at a pH of 4.5, so the system aims at maximum complexation of the aluminium ion by oxalic acid. Always an aluminium hydroxide precipitate must be present to obtain a removal completely in agreement with the proposed mechanism.

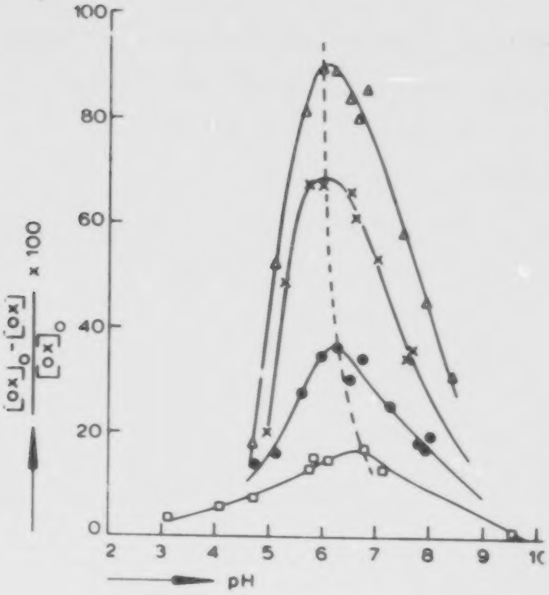


Fig. 14 The relative removal of oxalic acid as a function of the pH and the concentration of aluminium salt;
: $[Al'] = 10^{-4}$M; O: $[Al'] = 2.0 \times 10^{-4}$M; x: $[Al'] = 4.1 \times 10^{-4}$M;
: $[Al'] = 6.2 \times 10^{-4}$M

The experiments with o-phthalic acid are presented in Fig. 15. From this figure it can be concluded that the optimum pH for removal is about 6.4. This indicated that o-phthalic acid is removed by adsorption of free ions on a flox of aluminium hydroxyde. The complexation does not play an important part in this case.

Finally, the experiments with 1,3,5-benzene tricarboxylic acid are presented in Fig. 16. This figure shows an optimum removal at a pH of about 4.7, independent of the concentration of aluminium salt. This indicates a removal via an insoluble complex.

Concluding it can be said that dicarboxylic acid, produced during ozonization, can be removed in a secondary coagulation step. The acids are removed via the proposed mechanisms. The mechanism for removal can be predicted when the strength and the solubility in water of the produced complexes are known.

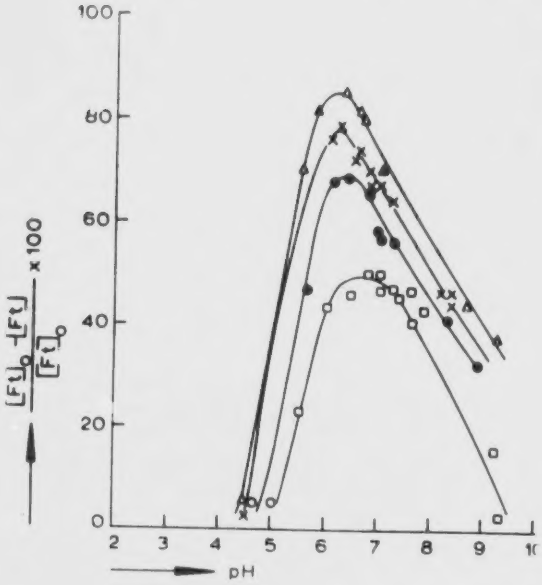


Fig. 15 The relative removal of o-phthalic acid as a function of the pH and the concentration of aluminium salt;
: $[Al'] = 1.8 \times 10^{-4}$M; O: $[Al'] = 4.4 \times 10^{-4}$M;
x: $[Al'] = 9.3 \times 10^{-4}$M; : $[Al'] = 1.8 \times 10^{-3}$M

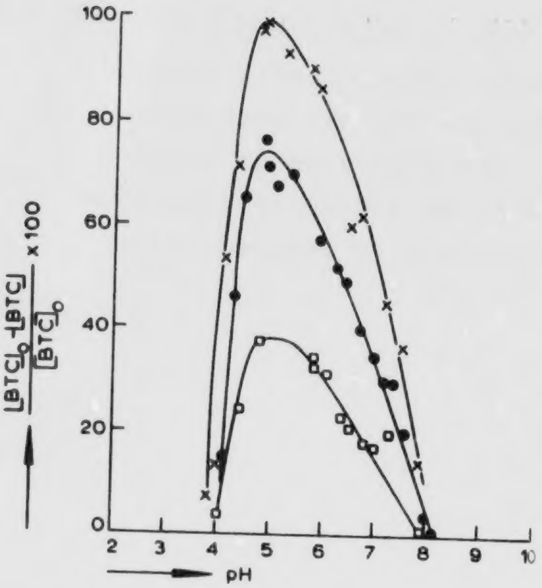


Fig. 16 The relative removal of 1,3,5-benzenetricarboxylic acid as a function of the pH and the concentration of aluminium salt;
: [Al']= 1.8x10^{-4}M; O: [Al']= 4.5x10^{-4}M;
x: [Al']= 8.9x10^{-4}M

Summary

In this paper the reaction of ozone with phenol, naphthalene and phenanthrene is reported. Mainly the production of stable peroxides and carboxylic acids has been investigated. When ozonizing phenol and phenanthrene only hydrogen peroxide is produced. The ozonization of naphthalene shows the production of hydrogen peroxide as well as an organic peroxide. This peroxide (a 1,2-dioxane derivate) is very stable in the absence of ozone. Additional supply of ozone to all reaction mixtures will result in the production of carboxylic acids, such as oxalic acid, phthalic acid, diphenic acid, etc.

The second part of the paper deals with the removal of

carboxylic acids by coagulation. Some models are presented by which the removal can take place. Oxalic acid is removed via adsorption of aluminium oxalate complexes on a floc of aluminium hydroxyde; phthalic acid is removed by adsorption of free phthalate ions on a floc of aluminium hydroxyde, and benzene tricarboxylic acid is removed as an insoluble complex.

(1) KRUITHOF, J.C.
Thesis Delft (1978)

(2) MEYERS, A.P.
Quarterly reports KIWA/RIWA Research (1972-1975), 1-11

(3) v.d. LEER, R.C., v.d. MEENT, W.
Quarterly Reports KIWA/RIWA Research (1975-1976), 12-14

(4) BAUCH, H., BURCHARD, H., ARSOVIC, H.M.
Gesundh. Ing. 9 (1970), 258

(5) EISENHAUER, H.R.
J. WPCF 40 (1968), 1887

(6) EISENHAUER, H.R.
J. WPCF 43 (1971), 200

(7) EISENHAUER, H.R.
Water Res. 5 (1971), 467

(8) GOULD, J.P.
Thesis Michigan (1975)

(9) GOULD, J.P., WEBER, W.J. jr.
J. WPCF 48 (1976), 47

(10) BAILEY, P.S., GARCIA-SHAPR, F.J.
J. Org. Chem. 22 (1957), 1008

(11) BAILEY, P.S., BATH, S.S., DOBINSON, F., GARCIA-SHARP, F.J., JOHNSON, C.D.
J. Org. Chem. 29 (1964), 697

(12) JOHNSON, C.D., BAILEY, P.S.
J. Org. Chem. 29 (1964), 709

(13) STURROCK, M.G., CRAVY, B.J., WING, V.A.
Can. J. of Chem. 49 (1971), 304

(14) SCHMITT, W.J., MORICONI, E.J., O'CONNOR, W.F.
J. Am. Chem. Soc. 77 (1955), 5640

(15) BAILEY, P.S.
J. Am. Chem. Soc. 78 (1956), 381

(16) BAILEY, P.S., MAINTHIA, S.B.
J. Org. Chem. 21 (1956), 1335

(17) STURROCK, M.G., CLINE, E.L., ROBINSON, K.R.
J. Org. Chem. 28 (1963), 2340

(18) SILLEN, L.G., MARTALL, A.E.
Stability Constants
Special Publication No. 17, Chem. Soc. London (1964)

(19) SILLEN, L.G., MARTELL, A.E.
Stability Constants, Suppl. No. 1, Special Publication No. 25, Chem. Soc. London (1972)

(20) SCHWARZENBACH, G., HELLER, J.
Helv. Chim. Acta 34 (1951), 576

(21) HEERTJES, P.M., KRUITHOF, J.C.
To be published

(22) WEAST, R.C.
Handbook of Chem. and Phys., 52th ed., The Chem. Rubber Co., Cleveland, Ohio (1971/1972)

(23) SECCO, F., VENTURINI, M.
J. Inorg. Chem. 14 (1975), 1978

MICROFLOCCULATION BY OZONE

D. Maier

1. Introduction

Although there is no doubt that ozone is neither a flocculating agent nor a precipitating agent in the conventional sense, but first and foremost an oxidizing agent, repeated mention is made in connection with ozonization of so-called microflocculation. All observations made up to now, given in a following chapter, show that the ozonized organic constituents of water acquire a special significance in the explanation of this phenomenon. For this reason, the known effects of ozone treatment on natural, organic water constituents will therefore be summarized.

2. Action of ozone on the organic constituents of water

In practically all publications relating to actual practice, purely phenomenological reports are found on the reduction of the water's colour, odour, and taste - an effect that can be directly perceived by the senses without resorting to measuring apparatus and analytical procedures. At least the alterations in colour, due to the ozone, can be evaluated quantitatively by a simple photometric process, and in the case of strongly coloured waters this can be done directly in the visible spectrum.

By extending the spectrum to the UV-absorption region further clear changes of the UV-spectra are observed, which in all cases studied so far show considerably lower extinction values than for non-ozonized water.

If the dissolved organic carbon, the content of which is hardly decreased by ozone treatment in the case of waters charged with natural constituents, is determined at the same time, the first guiding points become clear: in the first place ozonization does not bring about a quantitative oxidation of the water constituents to carbon dioxide but rather a chemical conversion of these constituents.

From a comparison of the chemical oxygen demand, measured before and after ozonization of organically loaded waters, it is found in addition that this chemical conversion is above all a conversion into polar constituents rich in oxygen. Simultaneous investigations of the molecular-weight distribution show that in ozonization this chemical conversion is accompanied by a reduction of the molecular weight.

Consideration of the reaction mechanisms cited in the literature (1,2) makes it evident that, depending on the pH, both electrophilic additions to any multiple bonds present, and radical attacks on the molecule are possible. For example, it can be clearly shown by infra-red spectroscopy of isolated ozonized water constituents (3) that ozonization leads to a strong attenuation of the double-bond character and the aromatic character, while simultaneously an increase in the contents of hydroxyl, carbonyl, and carboxyl groups is noticeable by the greater intensity of the corresponding absorption bands.

Several recently developed methods for the determination of organic acids (4-6) indicate on the basis of many experiments with various waters that the carboxyl groups produced during ozonization hold quantitatively the key position in the formation of new functional groups.

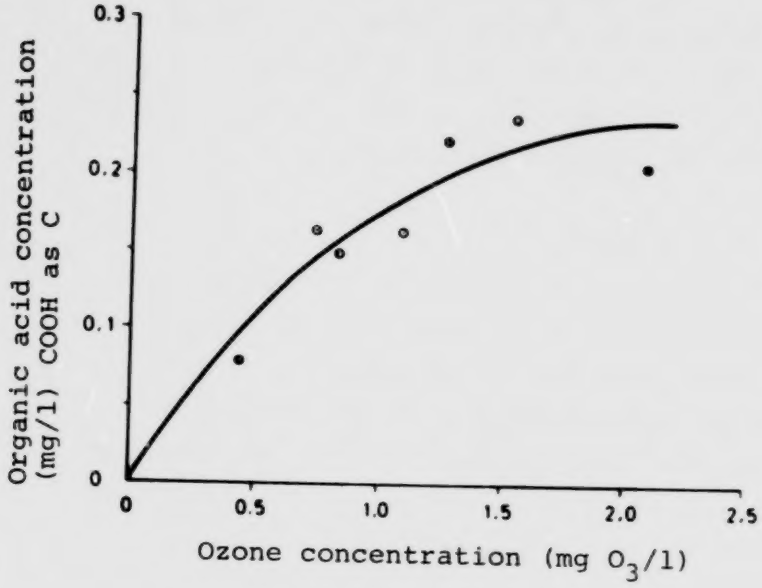


Fig. 1 Formation of organic acids during the ozonization of natural organic water constituents

By titration of slightly enriched water components in a quasi-anhydrous medium with tetrabutylammonium hydroxide, an increase in the -COOH groups in dependence on the ozone concentration could be observed on the example of the water of Lake Constance, as shown in Fig. 1. According to this figure, it is still possible to oxidize about 20% of the carbon atoms in the molecule to additional -COOH groups by means of ozonization.

This also explains why according to an analytical method recently developed by Maier (7) for the characterization of dissolved organic water constituents, essentially more decarboxylable carbon dioxide is formed after ozonization than before it.

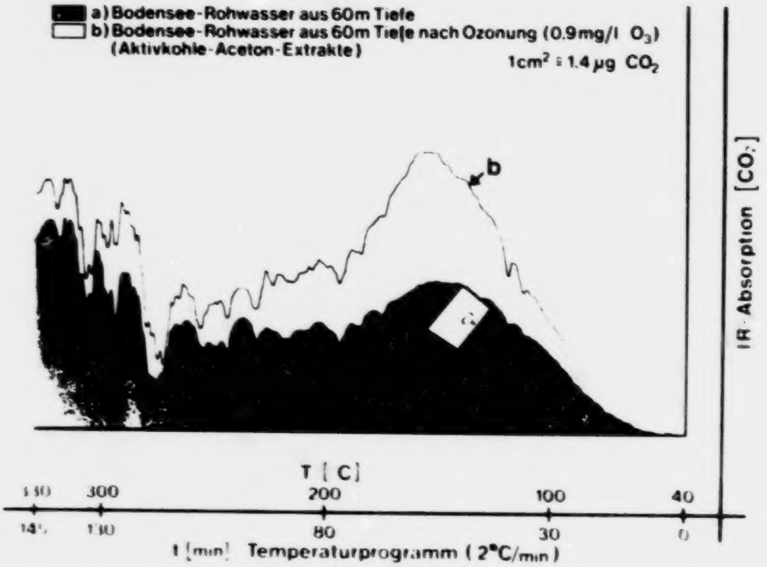


Fig. 2 Decarboxylation of organic water constituents

a) raw Lake Constance water from a depth of 60 m;
b) raw Lake Constance water from a depth of 60 m after ozonization (0.9 mg O_3/l)
(activated carbon-acetate extracts) 1 cm^2=1.4 µg CO_2

The decarboxylation spectrum reproduced in Fig. 2 shows in the higher temperature range, in which intramolecular oxidation processes play a part, that more active oxygen available for reaction is present in the ozonized than in the non-ozonized material.

This may also be why a shift of the oxidizability to more readily oxidizable compounds can be seen with ozonization in the temperature-programmed wet oxidation of ozonized organic water constituents, as shown in Fig. 3, which is based on the work of Weindel and Maier (8).

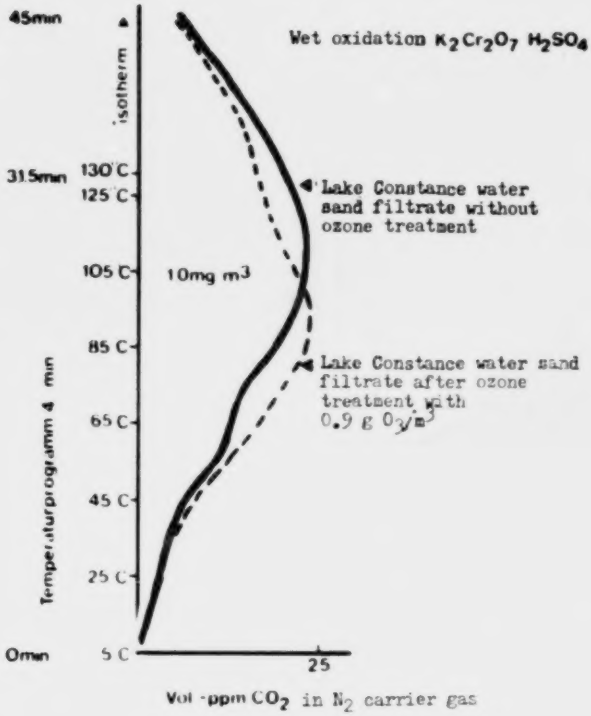


Fig. 3 Oxidation spectra of organic substances in Lake Constance water. Influence of O_3 treatment

3. Selected effects of ozone-induced type alteration of organic substances on practical treatment of drinking water

3.1. Toxicity and repopulation with bacteria

All the molecular properties altered by ozonization exhibit clear effects in the practice of drinking water treatment. These too should be given in summarized form.

In the first place it should be mentioned that ozonization does not produce any material more toxic than those already present in the water.

The strongest evidence (9) for this is the fact that sterile water, treated with various ozone concentrations and having a content of about 1.2 mg C/l of organic carbon, tends increasingly towards bacterial regeneration after the addition of a bacteria-containing water with increasing ozone concentration. This effect, desirable in the purification of waste water and already practised in some plants, indicates that ozonization leads to the formation of less toxic substances better utilizable by the bacteria. It is now also known that this so-called bacterial repopulation is only observed in waters with a sufficiently high content of organic carbon, according to the literature usually in excess of 0.5 mg C/l.

Maier's investigations (10) on the problem whether humic acids are made toxic by ozone treatment, with Daphnia pulex as the test organizm, also show clearly that, at any rate in the case of the humic acids of Lake Constance water, no toxic substances are produced by ozonization.

3.2. Chlorine consumption and haloform formation

For practice at least equally significant is the clearly demonstrated fact that the chlorine consumption of water charged with organic material is essentially slowed down by preliminary treatment with ozone, and consequently during the subsequent chlorination a smaller amount of organic chlorine compounds is formed (11). This can be clearly observed by investigating the chloroform formation in waters ozonized to different degrees. According to the work of Stieglitz et al. (12), some waters after ozonization have an increased content of particularly the readily volatile organic chlorine compounds. Since the possibility of oxidation of chloride to chlorine by ozone can be ruled out, this can only mean that organically bound chlorine is already present in the material at the start, and that the ozonization transforms it into compounds of lower molecular weight, i.e. smaller, more volatile, and capable of determination by gas chromatography.

4. Observations on microflocculation

4.1. Review of the literature

The described change in the type of the organic water constituents due to ozone is an essential prerequisite for understanding the microflocculation associated with ozonization.

For example, Gomella (13) has given a comprehensive report on the use of ozone in France, stating that in certain special cases the flocculation of colloidal organic substances occurs, e.g. in the case of strongly coloured, humic-acid-containing waters.

Gomella and Hallopeau (14) further assume that the flocculation is due to partial destruction of organic macro-protective molecules of natural origin, and conclude that this effect could help to reduce the amounts of conventional flocculation agents used. Taylor (15) also believes that by treatment with ozone the organic constituents of water are changed in such a way that during the subsequent flocculation with iron or aluminium salts the quantity of the flocculating agent required could be reduced.

In a detailed paper on the removal of iron from ground water, on the other hand, Cromley and O'Connor (16) describe the gelling action of ozonized organic substances, which prevents the flocculation of iron if the dissolved organic substances have not been largely decomposed.

In the treatment of the water of Lake Constance to supply the town of St. Gallen with drinking water, Grombach (17) regards it essential to follow the ozonization by a filtration stage, since "during oxidation a slight turbidity is produced, due to the precipitation of dissolved material".

The findings of Campbell and Pescod are also of interest (18); after ozonization of micro-filtered Scottish lake water, these authors observed the formation of an organic foam on the water surface, the amount of this foam increasing with increasing colour of the water, i.e. with increasing content of humic acids.

In studies on the removal of bacteria from a severely polluted stream with ozone, Franz and Gagnaux (19) observed a marked after-turbidity in the ozone-gasification chamber, which exerted an unfavourable effect on the removal of the bacteria.

The authors assume that the bacteria become encapsulated in the precipitated microflocculated material and so avoid being attacked further by the ozone.

Rohrer (20) claims that any peptides present in the water are flocculated by ozone, and that clay minerals are also rendered flocculatable to a large extent by an ozone treatment.

In a treatment of surface water described in a French Patent (21), the so-called M.D. process, after micro-filtration ozonization is used to bring about micelle formation, i.e. the occurrence of organic turbidity, which is removed by "demicellization", i.e. by flocculation with aluminium sulfate, in a subsequent sand filtration stage.

From a spring water containing humic substances Kopecky (22) isolated, after treatment with ozone, membrane-filterable organic compounds which he described as "ozonides" and which were shown to be bactericidal after their application to culture media inoculated with bacteria.

Rempel and Summerville (23) also observed increased turbidity after the ozonization of a surface water.

While this literature survey is essentially limited to the cases in which increased turbidity of a predominantly organic nature appeared after ozonization, there are also certain indications that turbidity present initially in water can be reduced by treatment with ozone.

Sontheimer (24) was the first to show, in fundamental experiments on the ozonization of Lake Constance water, a clear reduction of the particle count on the addition of ozone, which he attributed to an agglomeration of the smallest particles into micro-flocks.

"Ozone has a precipitating action" claims Kulcsar-Mescery (25), mentioning at the same time that fine clay suspensions, iron, manganese, humic substances, and other colloidal impurities are precipitated.

O'Donovan (26) studied the use of ozone in three Irish lake waters, and in the analysis of the ozone-treated waters established that their turbidity is normally lower than that of raw water.

In investigations on the filtration of suspended matter from Lake Constance water, Wagner, Keller and Müller (27) found that the suspended matter can be more efficiently removed by preliminary ozonization of the water, independently of the turbidity of the raw water; in the dosage range studied, between 0.5 and 2.3 g ozone/m^3, the amount of ozone used had no effect on the result. With the simultaneous use of flocculation agents (aluminium sulphate) in these experiments it could also be demonstrated that to achieve the same degree of removal of the suspended matter the ozonized water required less of the flocculation agent than non-ozonized water. The authors came to the conclusion "that as a result of ozonization an improvement in the flocculation and filtration capacity of colloidal substances is obtained". This may be due to the flocculation effect that occurs in the ozonization of humic-type organic substances.

Similar findings were reported by Wurster and Werner (28), who in the treatment of Danube water observed an optimal removal of very fine suspended particles by means of rapid filtration with the combined use of secondary flocculation and ozonization.

The literature evaluation of this problem was conducted as extensively as possible. It is already becoming evident that, according to the described experience gained in the practice of drinking water treatment, more than one mechanism can be made responsible for the so-called micro-flocculation, as indicated by the following experimental results - both our own and those selected from the literature.

4.2. Selected experimental results on micro-flocculation

In the ozone treatment of micro-filtered water of Lake Constance a situation is observed at certain times of the year - mostly in the summer during intensive production of algae and a perceptible increase in the organic products of algal metabolism - that can be characterized purely optically by an increased foam formation on the water surface in a reaction tank after the ozonization stage.

This situation, shown in Fig. 4, can be explained by flotation processes of suspended matter newly formed during the ozonization.

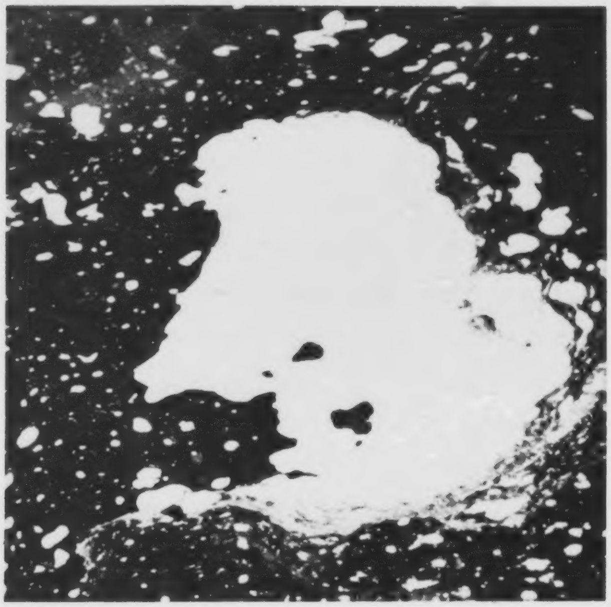


Fig. 4
Foam formation after ozonization of Lake Constance water

TABLE 1 Analysis of the "flotation foam" after ozonization of Lake Constance water on Nov. 28, 1977

Parameter	Percentage proportion of dry foam
Organic substance as loss on ignition 700°C/(1000°C)	40 / (43)
Acid insoluble components as SiO_2	29
Calcium	7.9
Magnesium	1.1
Aluminium	6.5
Iron	2.1
Manganese	0.5
Phosphorus as PO_4^{-3}	0.6
Zinc	0.2
Total trace elements (Hg, Se, As, Pb, Cd, Cr, Co, Ni)	0.04
Carbonate, calculated from Ca	11.9
Sulphate	not detectable
Nitrate	not detectable
Chloride	not detectable
Total	99.8

Analysis of this foam, given in Table 1, shows clearly that the main component is organic and that the original supposition of a high proportion of calcium carbonate does not correspond to the observed facts.

Table 1 shows, in addition, a considerable proportion of silica, presumably due to the shells of smaller silicic algae passing through the microfilter.

An additional check on the water body after every stage of the treatment of the Lake Constance Water Supply Association shows, with the aid of Fig. 5, that the freeze-dried filterable solids (TR), by the method described by Geller (29), increase by about 20% after direct contact with ozone, and in the next downstream intermediate tank are concentrated on the surface, in addition to the enrichment already mentioned.

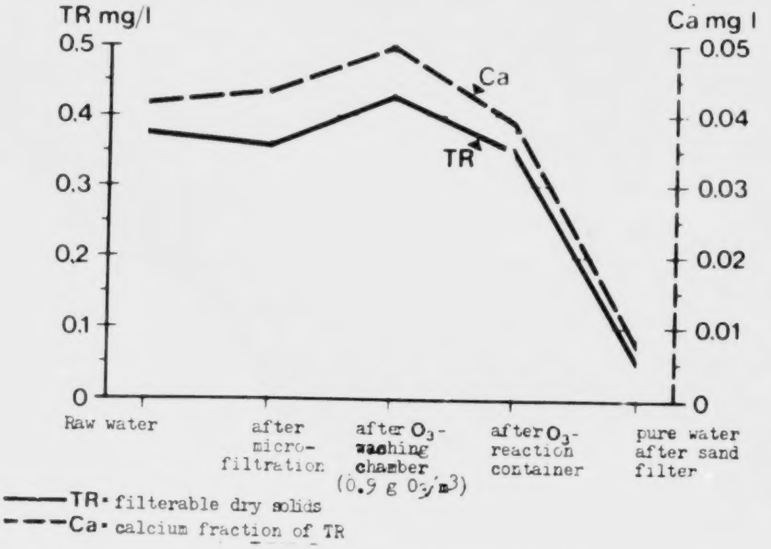


Fig. 5 "Microflocculation" in the treatment of Lake Constance water

The proportion of calcium, determined from the filterable solids, corresponds in order of magnitude to the values obtained in Table 1; a stoichiometric check shows that this is not precipitation of calcium carbonate.

What is much more likely is that a small proportion of the organic acids formed after ozonization is precipitated in the form of calcium salts.

These first observations on micro-flocculation suggest that the above situation, which often occurs in lake waters and has so far been unexplained, is somehow connected with the phytoplankton content of the water and its metabolic products.

The following figure indicates that the metabolic products of the phytoplankton probably play the leading role.

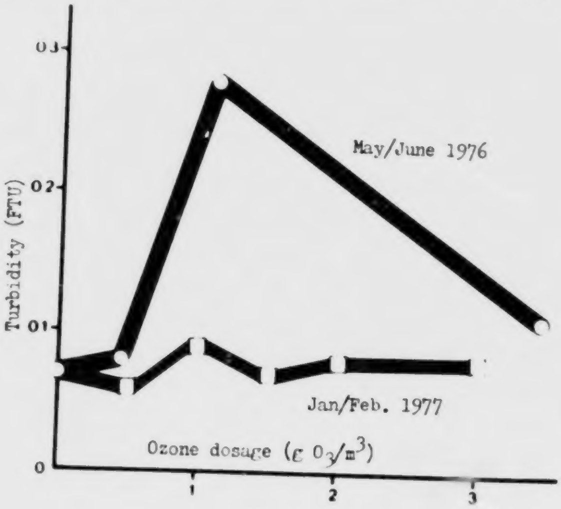


Fig. 6 Dependence of microflocculation in sand-filtered Lake Constance water from a depth of 60 m on the type of dissolved organic water constituents

In this experiment both phytoplankton and zooplankton had been eliminated as a start by intensive sand filtration. Microscopic examination of the starting water showed an alga-free filtrate with very good turbidity values of 0.07 formazine-turbidity units. Only in water with a high initial plankton content could larger turbidity increases due to ozone treatment be observed, while in the water from full circulation of the lake, with a low initial alga content, practically no turbidity increase occurred at all ozone concentrations. It must be emphasized that the turbidity values cannot be changed by acidification of the water with nitric acid or hydrochloric acid, so that here too the influence of calcium carbonate can be excluded.

It can also be seen from Fig. 6 that in the summer there is an additional optimum of the ozone concentration, at which these increases in turbidity occur.

If we start out from a water rich in inorganic turbidity but low in plankton, then, as Fig. 7 shows, the initial turbidity decreases with increasing dose of the ozone up to a concentration of about 1.5 mg O_3/l.

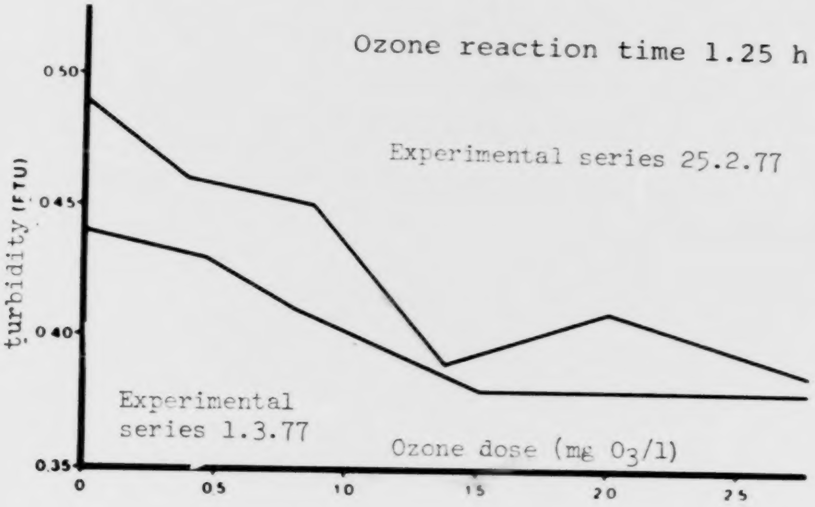


Fig. 7 Change in the raw water turbidity in dependence on the ozone concentration

Similar results were obtained by Schalekamp (30), who reported on the example of Lake Zürich water that ozone reduced the turbidity by about 20 - 40%, depending on the amount used. To gain a better understanding of the flocculating action of ozone, in the case of these Zürich investigations the particles were counted by size classes before and after the ozonization.

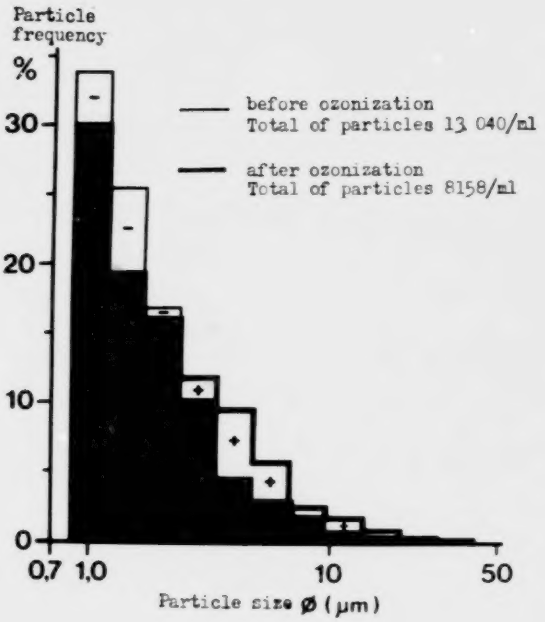


Fig. 8

Microflocculation in the treatment of Lake Zurich water (after M. Schalekamp)

As can be seen from Fig. 8, the smaller particles are reduced after ozonization with 1 mg/l, while the larger particles increase. Before the ozonization the total number of all particles with a mean diameter of 2.35 µm was 13,040 and after ozonization, with a larger mean particle diameter of 2.97 µm, it was only 8158. In ozonization with 2.5 mg O_3/l the same phenomenon can be detected, but much more weakly.

Still higher ozone concentrations invert the picture, so that after ozonization more particles are present than before.

These examples, cited from the practice of drinking water treatment, make it clear that two opposing processes are at work here, which make the interpretation of the phenomenon of micro-flocculation considerably more difficult.

The input of energy into the water must also be regarded as a factor influencing the formation of micro-flocculation. With varied conditions of operation of a container into which the ozonized water is introduced for a secondary reaction, by changing the proportions of the potential energy $E = g \cdot h$ and kinetic energy $E = 1/2\ m \cdot v^2$, the remaining water properties remaining constant, a manipulatable change in turbidity can be produced, as shown in Fig. 9.

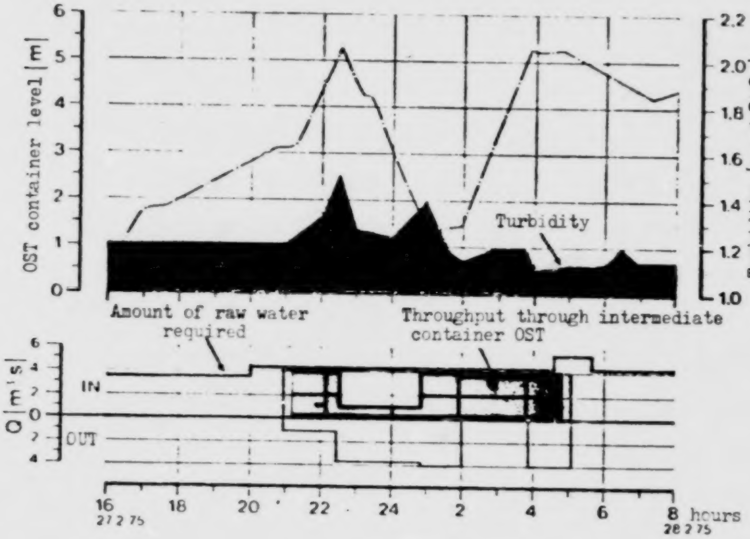


Fig. 9 Microflocculation in ozonized Lake Constance water

Since in this example too no precipitate of calcium carbonate can be detected analytically, which could be easily accounted for by the different turbulence within the container, it is certain that the turbidity changes observed are due solely to the superimposition of two opposing processes and their dependence on the energy input.

4.3. Results from model experiments

There is no doubt that in the interpretation of experimental results of this kind in practice which, as already mentioned, also depend on the season and on the general limnological state of the waters, a somewhat unsatisfactory feeling almost of uncertainty is obtained. It therefore is absolutely necessary to confirm the results relating to actual practice by aimed model experiments. The main difficulty in an effort of this kind lies in achieving comparability of the experimental conditions between the practice trial and the model experiment, which is of special significance in the case of the organic water constituents.

We now know that it is not possible to characterize the natural organic constituents of a surface water so precisely that a synthetic aqueous solution of these could be made up. Therefore, the preparation of model solutions is always directed at the enrichment and isolation of these substances which during the enrichment phase are changed by chemical reactions with one another or by redox processes in such a way that the isolated substance is no longer identical with the substance originally present (7).

This fact alone explains why until now it has only been possible in a few cases to achieve by means of ozone treatment a perceptible increase in turbidity on a model water, enriched with 30 mg/l of hymatomelanic acid, and hence a conversion of the dissolved substances into the colloidal state, as shown in Fig. 10.

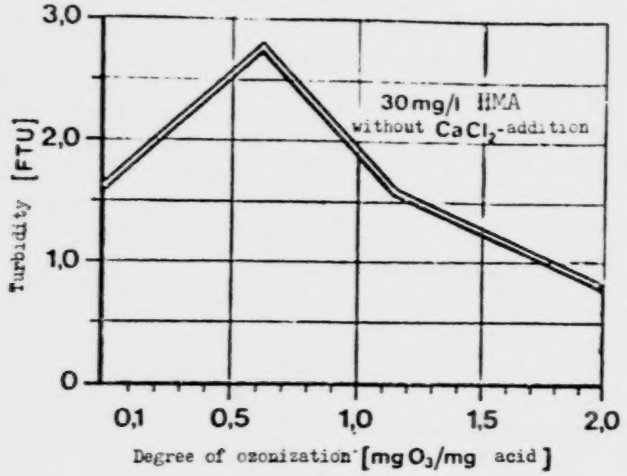


Fig. 10 Microflocculation of hymatomelanic acid (HMA) by O_3 (after R. Kurz)

The opposite effect, i.e. a reduction of the turbidity of a particle-rich water enriched with humic acid by ozone treatment, has been repeatedly demonstrated, as Kurz's results with kaolin suspensions (31) show in Fig. 11.

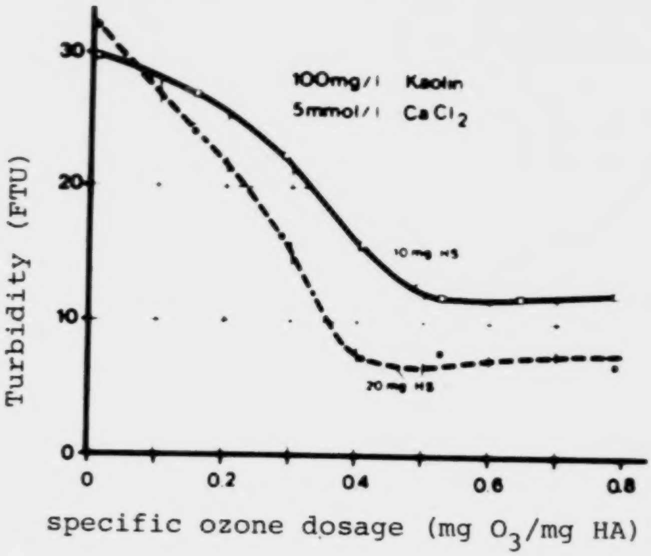


Fig. 11

Destabilization of a kaolin suspension by Lake Constance humic acids (HA) after ozone treatment

To explain these relationships in the two model trials, differing from the relationships observed in practice, we can only assume that in the formation of filterable substances which increase the turbidity (case 1) from dissolved substances, in the first place the entire molecule structure plays the decisive part, while the turbidity-diminishing action (case 2) depends mainly on the number and type of the functional groups and less on the basic skeleton of the carrier molecule. To the first case is added the possibility of the formation of insoluble alkaline earth metal salts, which is also structure-dependent. Summarizing case 1, it must be emphasized that in contrast to true flocculation, these processes should be regarded rather as precipitation reactions.

Case 2 can be explained by the ozone action on organic water constituents described in the first chapter: non-ozonized humic acids are adsorbed on the mineral particles forming the turbidity and endow them with an increased suspension capacity by a kind of protective-colloid action. If the polarity of the organic water constituents is increased by the ozonization, which manifests itself in a considerable increase in the number of carboxyl groups, while on the other hand the size of the molecule is decreased, the adsorption capacity on the turbidity particles immediately rises. At the same time, however, after ozonization substances are more strongly adsorbed on the turbidity material which, owing to their greater number of functional groups, now has essentially greater possibilities for cross-linking by bridge-formation. The fact that this "polyelectrolyte character" of ozonized organic constituents is noticeable even with a relatively small dose of ozone, and in the case of the humic acids of Lake Constance reaches its optimum with ozone doses between 0.8 and 1.0 mg/l, indicates that the molecular size and therefore also steric factors exert an influence that should not be neglected.

According to Stumm's classification of the agglomeration of colloidal particles, case 2 comprises true flock formation in which the destabilization mechanism is designated as flocculation.

5. Summary

Ozonization of the organic constituents of water gives rise to more polar compounds richer in oxygen and poorer in double bonds, with increased numbers of hydroxyl, carbonyl, and carboxyl groups and lower molecular weights. This ozone-induced change in structure is performed by two simultaneous and opposing processes.

The first case - the production of precipitating products from originally dissolved organic compounds - is probably strongly dependent on the structure of the entire molecule.

This includes the precipitation of insoluble alkaline earth metal salts of organic acids. Particularly in the case of lake waters there are indications that special metabolic products of the phytoplankton are made precipitable by ozonization. This phenomenon is observed in practice as a turbidity increase after ozonization.

The opposing process - destabilization of turbid suspensions by ozonized organic water constituents - should clearly be regarded as true flocculation, the ozonized organic substances adsorbed on the turbidity particles contributing by bridge-formation to cross-linking of the particles as a result of their polyelectrolyte character. A decisive part is played here not so much by the entire structure of the organic constituents as by the nature and quantity of their functional groups.

In water-treatment practice the two processes presumably take place in opposing directions and, in addition, are dependent on turbulence. The reported investigations are partly the results of a research programme on the optimization of the ozone process, promoted by the Water Economy Board. Some of the methods of characterizing organic water constituents were newly developed within the framework of a research programme, promoted by Dechema, for influencing corrosion processes with the aid of organic water constituents.

(1) AUTORENKOLLEKTIV
Organikum, Organisch-Chemisches Grundpraktikum: Ozonisierung
VEB Deutscher Verlag der Wissenschaften, Berlin (1970), 295-299

(2) REICHERTER, U.-F.
Untersuchungen über die Anwendung von Ozon bei der Wasser- und Abwasserreinigung
Dissertation, Fakultät für Chemieingenieurwesen, Universität Karlsruhe (1973)

(3) MAIER, D.
Wirkung von Ozon auf gelöste organische Substanzen
Vom Wasser 43 (1974), 127-160

(4) EBERLE, S.H., SCHWEER, K.H.
Bestimmung von Huminsäure und Ligninsulfonsäure im Wasser durch Flüssig-Flüssigextraktion
Vom Wasser 41 (1973), 27-44

(5) MAIER, D., FUCHS, F., SONTHEIMER, H.
Bestimmung von organischen Säuren in Wässern und auf Aktivkohle
gwf-Wasser/Abwasser 117 (1976), 2, 70-74

(6) WAGNER, I., HOYER, O.
Die Bestimmung von Huminsäuren und Ligninsulfonsäuren in Wässern mittels UV-Spektroskopie
Vom Wasser 45 (1975), 207-216

(7) MAIER, D.
Temperaturprogrammierte Decarboxylierung organischer Wasserinhaltsstoffe
Vom Wasser 50 (1978) (in press)

(8) WEINDEL, W., MAIER, D.
Das Oxydationsspektrum, eine analytische Hilfe zur Beurteilung von Verfahrensschritten der Wasseraufbereitung
Vom Wasser 50 (1978) (in press)

(9) MAIER, D., KURZ, R.
Untersuchungen zur Optimierung der Ozonanwendung bei der Aufbereitung von Seewasser
Veröffentlichungen "Internationales Symposium Ozon und Wasser" Wasser Berlin 77 (1977), 211-232

(10) MAIER, D.
Werden Huminsäuren durch Ozonbehandlung toxisch?
Vom Wasser, 51 (1979) (in press)

(11) MAIER, D., MÄCKLE, H.
Wirkung von Chlor auf natürliche und ozonte organische Wasserinhaltsstoffe
Vom Wasser 47 (1976), 379-397

(12) STIEGLITZ, L., ROTH, W., KÜHN, W., LEGER, W.
Das Verhalten von Organohalogenverbindungen bei der Trinkwasseraufbereitung
Vom Wasser 47 (1976), 347-377

(13) GOMELLA, C.
Ozone Practices in France
J. AWWA 64 (1972), 1, 39-45

(14) GOMELLA, C., HALLOPEAU, J.
Progrès sur la recherche sur les effects de l'ozone sur l'eau pendant le traitement et dans le rèseau de distribution
Publication 9th IWSA Congress New York (1972), 20-24

(15) TAYLOR, E.J.
Weshalb Philadelphia Ozon nahm
Translation from "The American City Magazine" (1949)

(16) CROMLEY, J.T., O'CONNOR, J.T.
Effect of Ozonation on the Removal of Iron From a Ground Water
J. AWWA 68 (1976), 315-319

(17) GROMBACH, P.
Die neue Ozonanlage des Bodensee-Trinkwasserwerkes der Stadt St. Gallen
Monatsbulletin SVGW 48 (1968), 7, 211-215

(18) CAMPBELL, R.M., PESCOD, M.B.
The Ozonization of Turret and Other Scottish Waters
Water and Sewage Works 113 (1966), 7, 268-272

(19) FRANZ, J., GAGNAUX, A.
Entkeimung mit Ozon unter besonders hohen Anforderungen
Wasser, Luft und Betrieb 15 (1971), 11, 393-396

(20) ROHRER, F.
Ozon und seine Verwendung zur Wasseraufbereitung
Schweizer Brauerei-Rundschau 63 (1952), 135-155

(21) DIAPER, E.W.J.
A new method of treatment for surface water supplies
Water and Sewage Works 117 (1970), 11, 373-378

(22) KOPECKY, J.
Erfahrungen mit der Ozonisierung
Fortschritte der Wasserchemie 7 (1967), 94-100

(23) SUMMERVILLE, R.C., REMPEL, G.
Ozone for Supplementary Water Treatment
J. AWWA 64 (1972), 377-382

(24) SONTHEIMER, H.
Erfahrungen beim Einsatz von Ozon in der Trinkwasseraufbereitung; 3. Ozon als Oxidations- und Flockungshilfsmittel
Wasserfachliche Aussprachetagung des DVGW/VGW in Wiesbaden (1971), Sonderdruck DVGW-Broschüre "Wasseraufbereitung-Wasserzähler"

(25) KULCSAR-MESCERY, J.
Wasseraufbereitung durch Ozonisierung
Gas, Wasser, Wärme 9 (1955), 8, 193-195

(26) O'DONOVAN, D.C.
Treatment with Ozone
J. AWWA (1965), 9, 1167-1194

(27) WAGNER, I., KELLER, H., MÜLLER, R.
Untersuchungen zur Aufbereitung von Bodenseewasser mittels Ozonung und Flockungsfiltration
gwf-Wasser/Abwasser 118 (1977), 320-322

(28) WURSTER, E., WERNER, G.
Die Leipheimer Versuche zur Aufbereitung von Donauwasser
gwf-Wasser/Abwasser 112 (1971), 81-90/193-199

(29) GELLER, W.
Zur gravimetrischen Bestimmung des Suspensagehaltes von Gewässern
7. Bericht der Arbeitsgemeinschaft Wasserwerke Bodensee-Rhein (1975), 146-151

(30) SCHALEKAMP, M.
Die Erfahrungen mit Ozon in der Schweiz, speziell hinsichtlich der Veränderung von hygienisch bedenklichen Inhaltsstoffen
gwf-Wasser/Abwasser 57 (1977), 9, 657-673

(31) KURZ, R.
Untersuchungen zur Wirkung von Ozon auf Flockungsvorgänge
Dissertation, Fakultät für Chemieingenieurwesen, Universität Karlsruhe (1977)

PRACTICAL USES OF OZONE IN DRINKING WATER TREATMENT

R.G. Rice, C.M. Robson, G.W. Miller and A.G. Hill

Abstract

Ozone has been used continuously for the treatment of drinking water since 1906 in the city of Nice, France, where it was first installed for disinfection purposes. Since 1906, the uses of ozone for water treatment have grown to include various chemical oxidation processes, in addition to bacterial disinfection and viral inactivation. Applications for ozonation now include oxidation of inorganic materials (such as sulfides, nitrites, cyanides, ferrous and manganous ions), organic materials (such as phenolics, detergents, pesticides, taste and odor-causing compounds, color-causing organics, other soluble organics), turbidity or suspended solids flocculation (by changing the surface characteristics), microflocculation and recently to promote aerobic biological processes conducted in filter media. Each of these uses of ozonation is discussed in terms of their chemistries and extent of application in the more than 1,000 drinking water treatment plants known to be using ozonation, most of which are located in Europe.

1. History of Ozone Use in Water Treatment (1)

The earliest experiments on the use of ozone as a germicide were conducted by de Meritens in 1886 in France, who showed that even dilute ozonized air will effect the sterilization of polluted water. A few years later (1891), the bactericidal properties of ozone were reported by

Fröhlich from pilot tests conducted at Martinikenfeld in a drinking water treatment plant erected by the German firm of Siemens & Halske. In 1893, the first drinking water treatment plant to employ ozone was erected at Oudshoorn, Holland. Rhine River water was treated with ozone, after settling and filtration. Siemens & Halske next built treatment plants at Wiesbaden (1901) and Paderborn (1902) in Germany which employed ozone.

A group of French doctors studied the Oudshoorn plant and its ozonized water and, after pilot testing at St. Maur (in Paris) and at Lille, a 5 mgd plant was constructed at Nice, France (the Bon Voyage plant), which employed ozone for disinfection. Because ozone has been used continuously at Nice since the Bon Voyage plant began operating in 1906, Nice is referred to as "the birthplace of ozonation for drinking water treatment".

Full-scale water treatment plants then were constructed in several European countries. As of 1916 there were 49 treatment plants in Europe having a total capacity of 84 mgd (2) in operation, and 26 of these were in France. By 1940 the number of drinking water treatment plants throughout the world using ozone had risen to 119, and as of 1977 at least 1043 plants, mostly in Europe (Table 1) are known to be using ozone for drinking water treatment (3). As might be expected, most of the European drinking water treatment plants using ozone are in France, although Switzerland and Germany account for most of the remainder of the European plants.

In the United States, only one plant has been using ozone continuously since the early 1940s (Whiting, Indiana)(4,5). In 1973 the second U.S. plant to use ozone went on stream at Strasburg, Pennsylvania (6). The remaining three plants became operational in late 1977 or early 1978 (7).

TABLE 1 Operational plants using ozone - 1977

Country	Number of Plants
France	593
Switzerland	150
Germany	136
Austria	42
Canada	23*
England	18
The Netherlands	12
Belgium	9
Poland	6
Spain	6
USA	5
Italy	5
Japan	4
Denmark	4
Russia	4
Norway	3
Sweden	3
Algeria	2
Syria	2
Bulgaria	2
Mexico	2
Finland	1
Hungary	1
Corsica	1
Ireland	1
Czechoslovakia	1
Singapore	1
Portugal	1
Morocco	1
Total	1039

* Includes expansions. Actual number of operating plants in Canada = 20, with 3 more under construction.

The fact that the U.S. Environmental Protection Agency recently has proposed regulations for the larger U.S. water supply systems regarding control of organic chemicals in U.S. drinking water supplies has prompted a keen interest on the part of the North American water supply industry to know more about the uses of ozone and its engineering parameters than had been known in late 1974. In response to this interest, the U.S. EPA funded a survey, conducted by Public Technology Inc., of Washington, D.C., to assess the state-of-the-art of the use of ozone and of chlorine dioxide for the treatment of drinking water. This assessment involved a significant questionnaire survey of many European drinking water treatment plants, in which many of you participated. In May, 1977, the PTI survey team visited some two dozen European drinking water treatment plants using ozone and/or chlorine dioxide. In August 1977, the PTI survey team visited nine plants in the Province of Quebec, Canada. The present paper is taken from the results of this EPA-funded study.

2. Applications of Ozone in Water Treatment

Ozone is a powerful oxidant (Table 2). In acid solution, the oxidation potential of ozone (2.07 volts) is second only to that of elemental fluorine among the commonly used oxidants for drinking water treatment. Because many contaminants in raw water supplies are oxidizable, ozone can be and is being used for many different applications. The major uses for ozone in modern drinking water treatment processes are listed in Table 3. Although the early uses for ozone in treating drinking waters were predominantly for disinfection (bacterial kill and viral inactivation), today oxidative applications account for a significantly increasing number of installations.

TABLE 2 Oxidation-reduction potentials of water treatment agents[x]

REACTIONS	POTENTIAL IN VOLTS (E°) 25 °C
$F_2 + 2e = 2F^-$	2.87
$O_3 + 2H^+ + 2e = O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e = 2H_2O$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e = Cl^- + 2H_2O$	1.57
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.49
$HOCl + H^+ + 2e = Cl^- + H_2O$	1.49
$Cl_2 + 2e = 2Cl^-$	1.36
$HOBr + H^+ + 2e = Br^- + H_2O$	1.33
$O_3 + H_2O + 2e = O_2 + 2OH^-$	1.24
ClO_2 (gas) $+ e = ClO_2^-$	1.15
$Br_2 + 2e = 2Br^-$	1.07
$HOI + H^+ + 2e = I^- + H_2O$	0.99
ClO_2 (aq) $+ e = ClO_2^-$	0.95
$ClO^- + H_2O + 2e = Cl^- + 2OH^-$	0.9
$HO_2^- + H_2O + 2e = 3OH^-$ (basic)	0.87
$ClO_2^- + 2H_2O + 4e = Cl^- + 4OH^-$	0.78
$OBr^- + H_2O + 2e = Br^- + 2OH^-$	0.70
$I_2 + 2e = 2I^-$	0.54
$I_3^- + 2e = 3I^-$	0.53
$OI^- + H_2O + 2e = I^- + 2OH^-$	0.49
$O_2 + 2H_2O + 4e = 4OH^-$	0.40

[x] Handbook of Chemistry & Physics, 56th Edition, 1975-76. CRC Press Inc., Cleveland, Ohio, p. D-141-143.

TABLE 3 Applications of ozone in drinking water treatment

- Bacterial Disinfection
- Viral Inactivation
- Oxidation of Soluble Iron and/or Manganese
- Decomplexing Organically - Bound Manganese (Oxidation)
- Color Removal (Oxidation)
- Taste & Odor Removal (Oxidation)
- Algae Removal (Oxidation)
- Oxidation of Organics
  - Phenols
  - Detergents
  - Pesticides
- Microflocculation of Dissolved Organics (Oxidation)
- Oxidation of Inorganics
  - Cyanides
  - Sulfides
  - Nitrites
- Turbidity or Suspended Solids Removal (Oxidation)
- Pretreatment for Biological Processes (Oxidation)
  - On Sand
  - On Anthracite
  - On Granular Activated Carbon
- To Make Treated Water Blue

2.1 Bacterial Disinfection

The French have pioneered the use of ozonation for bacterial disinfection. Guinvarc'h (8) reported that ozonation at the Paris, France, St. Maur plant produced waters which never showed the presence of E. coli, although the raw Marne river waters at the time showed coliform counts of 15,000 to 100,000 units/liter, with average values of 30,000 to 50,000. O'Donovan (9) points out that for bacterial disinfection, the usual ozone dosage rate in water treatment plants at that time was 1.5 to 2 mg/l.

Miller et al. (3) have found that the current average ozone dosage rates in drinking water treatment plants are 1 to 4 mg/l today. Where preozonation treatment is non-existent or when loadings of ozone-demanding organic or inorganic materials are high, such as during pollution episodes, ozone doses much in excess of 2 mg/l can be required to attain the desired degree of bacterial disinfection. On the other hand, only 0.25 mg/l of ozone provided satisfactory disinfection at Boxley, England (10).

In addition, the bactericidal action of ozone is little affected by changes in temperature or pH, and the disinfecting action of ozone is virtually instantaneous. Weaker oxidants require more contact time (and usually higher concentrations) to provide the same degree of bacterial disinfection (9).

2.2 Viral Inactivation

In this application the pioneering work was conducted by French public health officials. Coin and his coworkers (11,12) used poliomyelitis virus Type I (1964) and Types II and III (1967) to demonstrate that when an amount of residual dissolved ozone equivalent to 0.4 mg/l can be measured after 4 minutes of continuous ozonation, the degree of viral inactivation surpasses 99.9 %.

Subsequent to this work in the late 1960s, the city of Paris adopted the 0,4 mg/l residual ozone after 4 minutes as a standard for the use of ozonation for viral inactivation. Currently this standard has been adopted throughout France (13).

In actual plant practice, in order to insure that these minimum ozonation conditions are met consistently, the French increase the ozonation time to at least eight minutes, and sometimes contact times of 12 minutes are employed. It is general French practice to use at least two ozone contacting chambers. In the first chamber the initial ozone demand of the water is satisfied and the residual of 0,4 mg/l of ozone is attained; in the second chamber the 0.4 mg/l of ozone residual is maintained. Satisfying the ozone demand of the water in the first contact chamber requires relatively large amounts of ozone, and some 67 % of the total ozone dosed is applied here. Lower amounts of ozone (about 33 %) are applied to the second chamber to maintain the 0.4 mg/l of dissolved ozone, usually for periods of 4 to 8 additional minutes.

At the present time, France is the only country known to have formally adopted these ozonation conditions as a treatment standard for viral inactivation. However, many plants in countries outside of France have designed ozonation contacting systems for disinfection which utilize the same treatment conditions (3). It is important to recognize that under these viral inactivation conditions of ozonation, bacterial disinfection also is obtained.

Ozonation of organic compounds usually produces oxygenated organic materials which are more readily biodegradable. In addition, ozonation does not readily oxidize ammonia except at high pH (above 9). For these reasons, ozonized waters containing these materials generally are treated with small dosages of chlorine, chlorine dioxide or chloramine to prevent bacterial regrowths in the distribution networks.

In Switzerland, it is common practice in many of the 150 drinking water treatment plants to follow ozonation with filtration through granular activated carbon in order to deozonize the water, then to add chlorine dioxide. Deozonation is considered necessary because of reactions between ozone and ClO_2 in aqueous solution (14). Masschelein (15) points out that ozonation of solutions of chlorine dioxide or sodium chlorite in the mg/l range produces chlorate stoichiometrically:

$$NaClO_2 + O_3 \longrightarrow NaClO_3 + O_2$$

The dimerization of ClO_2 to Cl_2O_4 is considered to be the first step in the ozonation process (16). The reaction is very fast and is almost controlled by the diffusion rate of ozone (17).

Many European, Canadian and the Strasburg, Pennsylvania, plants employ ozonation as the terminal treatment disinfection step, however, without aftergrowth problems. Miller et al. (3) have concluded that ozonation can be used as a terminal treatment step only if all of the following conditions are met simultaneously:

1) The distribution system must be clean and not subject to leaks,
2) Dissolved organic carbon concentrations must be less than 0.2 mg/l,
3) Ammonia must be absent,
4) Water temperature must be low and
5) Residence time in the distribution must be short (less than 1 day).

2.3 Oxidation of Soluble Iron & Manganese

Ferrous iron is oxidized rapidly by ozone to ferric ions, which then hydrolyze, coagulate and precipitate according to the following equations:

$$Fe^{+2} + O_3 \longrightarrow Fe^{+3}$$

$$Fe^{+3} + H_2O \longrightarrow Fe(OH)_3$$

Similarly, manganous ions can be oxidized to manganic ions, which then form insoluble manganese dioxide:

$$Mn^{+2} + O_3 \longrightarrow Mn^{+4}$$

$$Mn^{+4} + H_2O \longrightarrow Mn(OH)_4 \longrightarrow MnO_2$$

However, over-ozonation of manganous compounds produces the very water soluble permanganate ion, which is pink in color:

$$Mn^{+2} \text{ or } Mn^{+4} + O_3 \longrightarrow MnO_4^-$$

Permanganate is toxic and should be prevented from entering water distribution systems. Its presence in distribution networks can lead to buildup of MnO_2 scales. Permanganate can be produced (or used) in the water treatment plant but kept from entering distribution system networks by several procedures, all of which depend upon the fact that it is a very strong oxidant (see Table 2) with an oxidation potential of 1.68 volts, close to that of ozone.

Normally, ozonation of ferrous and manganous compounds is conducted early in the water treatment process and the hydrolyzed and precipitated inorganic hydroxides are filtered. If the filtered water is distinctly pink in color, the operator is alerted to the fact that he is using too much ozone, and the ozone dosage should be reduced. Tanks which provide 15 to 30 minutes of holding time are used in the Düsseldorf area. This allows the permanganate to oxidize dissolved organic materials, thereby being reduced to the insoluble manganese dioxide:

$$MnO_4^- + \text{organics} \longrightarrow MnO_2 + \text{oxidized organics}$$

Alternatively, the pink water can be filtered through granular activated carbon, where the permanganate is quickly reduced to MnO_2 in the first few centimeters of the bed or column. The insoluble dioxide then is removed during routine backwashing of the activated carbon medium.

2.4 Decomplexing of Organically-Bound Manganese

When iron and manganese are present as free inorganic cations, they can be oxidized readily by agents much weaker than ozone - simple aeration is known to be effective, for example. However, when manganese is present as organic complexes, as is the case when decaying vegetation is present, then even chlorine is not powerful enough to break down the manganese complexes. In such cases stronger oxidants, such as chlorine dioxide or ozone, are used, again as a preoxidation step so as to prevent the oxidized manganese from being passed into the distribution system.

2.5 Color Removal

Usually the colors in drinking water are derived from the decomposition of naturally occurring humic materials. Colors usually are caused by the presence of unsaturated organic moieties conjugated in the compounds (i.e., alternating double and single bonds). Compounds containing such conjugated groupings are referred to as chromophores.

Ozone is particularly reactive with unsaturated groups, cleaving the carbon-carbon double bonds to produce ketones, aldehydes or acids, depending upon the other substituents on the carbon atoms affected, the amount of ozone and contact conditions applied. As soon as the conjugation has been disrupted by oxidation, the color will disappear. This does not necessarily mean that all of the color-causing organic compound has been converted to carbon dioxide and water, however, but simply that the conjugated unsaturated groups responsible for the original color have been destroyed.

In industrial areas where textile manufacturing or dyeing is prevalent, organic dyestuffs sometimes are discharged from these industrial installations and are found in raw waters entering drinking water treatment plants. These dyestuffs generally are polycyclic, highly conjugated organic materials, easily decolorized by a powerful oxidizing agent such as ozone. As before, however, the decolorized water will still contain considerable dissolved organic carbon, which is readily biodegradable.

2.6 Taste and Odor Removal

As a general rule, taste and odor causing compounds are organic in nature, although many inorganic sulfides also are encountered which are highly odorous. Many of these organic compounds which cause unacceptable tastes and odors are formed from natural vegetation during anaerobic decomposition in the ground or in surface waters in which the dissolved oxygen content may be too low to support aerobic colonies. Examples of such materials include terpene derivatives, such as geosmine, and some alicyclic and/or aromatic alcohols. The latter are classed as phenols.

Odorous compounds containing unsaturation, such as phenols, usually are readily oxidizable by ozone. On the other hand, saturated organic compounds usually are oxidized only slowly by ozone. Since the amount of ozone required to remove tastes and odors will vary depending upon the specific offensive organic compounds present, it is essential to conduct pilot studies with ozonation to ascertain the most cost-effective relationship of ozone dosage and contact time to cope with the specific local problem. As before, destruction of organic compounds which cause tastes and odors by oxidation does not necessarily insure total oxidation of those organic compounds to CO_2 and water.

2.7 Algae Removal

During seasonal periods of climate changes and when the proper nutrient balances are present in the raw waters, algae growths are promoted. As these plants grow, their metabolism produces by-products which can cause offensive tastes and odors. In addition, the presence of large amounts of growing algae in the water treatment plant will clog filters, requiring more frequent backwashing. Ozonation will disrupt the metabolic processes of many types of algae by oxidizing the essential organic components. In treatment plants where ozonation already has been installed for other purposes (such as disinfection or iron and manganese oxidation), seasonal blooms of algae in the raw waters are handled simply by increasing the preozonation dosages until the bloom periods are completed. This requires installing sufficient ozone generation capacity initially to cope with this problem.

2.8 Oxidation of cyanides, sulfides and nitrites

Toxic cyanide ions are readily oxidized by ozone to the much less toxic cyanate ion:

$$CN^- + O_3 \longrightarrow CNO^-$$

At low or high pH, cyanate ion hydrolyzes to produce CO_2 and nitrogen:

$$CNO^- + H_2O \longrightarrow CO_2 + N_2$$

Sulfide ion is easily oxidized to sulfur, then to sulfite and, finally, to sulfate:

$$S^{-2} + O_3 \longrightarrow S^o \longrightarrow SO_3^{-2} \longrightarrow SO_4^{-2}$$

The degree of oxidation attained depends upon the amount of ozone employed and the contact time. Organic sulfides will oxidize to sulfones, sulfoxides and sulfonic acids upon ozonation at slower rates than the sulfide ion itself.

Nitrite ion is readily oxidized to nitrate ion by ozone:

$$NO_2^- + O_3 \longrightarrow NO_3^-$$

Organic nitrites, nitroso compounds, hydroxylamines and the like also will be oxidized, first to the corresponding nitro compounds. These then will decompose upon continued ozonation, liberating nitrate ions and carbonaceous compounds. As before, the degree of oxidation will depend upon the specific compounds present, the amount of ozone employed and the contacting conditions employed.

2.9 Oxidation of Organics

Although there are literally myriads of organic compounds present in water supplies (at the latest count, the U.S. EPA has identified over 700 individual organic compounds), not all are oxidized at the same rates upon ozonation. Indeed, many highly halogenated organic compounds are not oxidized at all under ozonation conditions normally encountered in drinking water treatment plants. Rice & Miller (18) discuss these aspects in reviewing the nature of organic oxidation products formed upon reaction with ozone under aqueous conditions.

During the PTI survey of drinking water plants using ozonation, many plants responding to the questionnaires reported that they are using ozone for "organics removal". However, in most cases the organics removed are not identified. Nevertheless, some specific organic materials known to be readily "removed" (oxidized) by ozone have been identified, and these include phenols, detergents and certain pesticides.

2.9.1 Phenols

Phenols, especially the non-chlorinated phenols, generally are readily oxidized upon ozonation. It is important to recognize, however, that destruction of the phenolic component requires much less ozone than conversion of all of the phenolic compound to CO_2 and water.

Eisenhauer (19) ozonized aqueous solutions of phenol for 30 minutes (until phenol was "destroyed" by the analytical test used) and isolated catechol, hydroquinone, p-quinone, cis-muconic acid, oxalic acid and fumaric acids as organic oxidation products. After 4 moles of ozone had been consumed per mole of phenol, substantially all of the phenol originally present had disappeared, but very little CO_2 had formed.

In later work, Eisenhauer (20) showed that as ozonation of phenol solutions proceeds, no CO_2 is formed until after 1.5 moles of ozone/mole of phenol is consumed. However, after 33 % of the theoretical CO_2 had formed, CO_2 production then ceased. He concluded that if destruction of the aromatic ring is sufficient to solve the particular local problem, then 98 % of the phenol can be "destroyed" using 5 moles of ozone per mole of phenol present. However, 67 % of the original carbon present in the phenol still is present in the form of other organic compounds which are oxidation products of phenol.

The oxidation of phenol itself proceeds first through di- and trihydroxyaromatic compounds and quinones. Continued ozonation breaks the aromatic ring, forming aliphatic acids, the most stable end product usually being oxalic acid.

Phenols with aliphatic substituents on the ring are first oxidized to benzoic acids, then to hydroxy benzoic acids, after which the aromatic rings are ruptured. As oxygenation proceeds, the oxidized intermediate compounds become more readily biodegradable.

Hillis (21) studied the oxidation of 14 phenols with ozone over the pH range 4 to 10. Starting with 30 mg/l concentrations of these phenols and ozonizing over 4 to 12 minutes, phenol concentrations were lowered to 0.10 mg/l. However, the corresponding COD values were lowered by only 50 %. This is further indication that although the specific phenol is destroyed by ozonation, oxidized organic products remain in solution.

Nevertheless, the elimination of measurable concentrations of phenols by ozonation is practised successfully at a great many drinking water treatment plants (3).

2.9.2 Detergents

Detergents generally fall into two classes, linear alkyl sulfonates and linear alkylbenzene sulfonates. There are some aliphatic quaternary amino compounds which are used as detergents, however, most household laundry detergents are of the first two types. The more readily biodegradable detergents will decompose in sewage treatment plants or in rivers and streams, given sufficient time. However, many raw water supplies are contaminated from time to time by detergents or their partial decomposition products.

As discussed earlier, those compounds containing aromatic groupings will be more readily oxidized by ozone, while the aliphatic materials will be less reactive. In addition, Gilbert (22,23,24) has shown that even aromatic compounds containing sulfonic acid groups will be less readily oxidized by ozonation than the same compounds without the sulfonic acid groupings.

Gilbert (23) also has shown that in ozonizing pure aqueous solutions of compounds over the pH range of 3 to 7, 1 kg of COD can be removed from solution with 1.2 kg of ozone. On the other hand, in more polluted wastewaters, 2 to 5 kg of ozone are required to remove 1 kg of COD from solution.

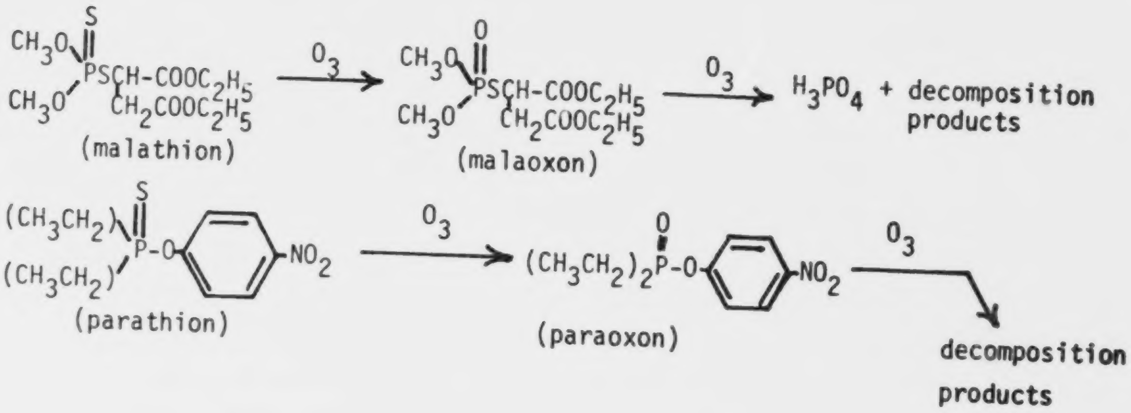
In addition, the excellent work of Hoigné (this meeting) and of Hoigné & Bader (25,26 and prior references cited therein) on determination of reaction rates of specific organic compounds with ozone will allow the practising water treatment plant engineer to ascertain the ease of oxidation of specific organic compounds that he may find in his raw waters.

When ozonation already has been installed in a water treatment plant for some other purpose, the presence of significant quantities of detergents in the raw water is easily recognized by the sudden foaming of the waters during preozonation or in the first contacting chamber when ozone is used for disinfection. In such instances merely increasing the ozone dosage usually copes with the problem. As with seasonal algae blooms, it is important that sufficient ozone generation capacity be available in the plant.

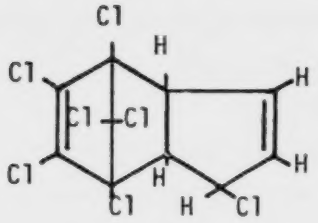
2.9.3 Pesticides

Pesticides cannot be classified so simply as to their reactivity with ozone. Phosalone and aldrin, for example, are readily oxidized to destruction with small amounts of ozone. On the other hand, dieldrin, chlordane, lindane, DDT, PCBs, PCP and endosulfan are only slightly reactive with ozone under normal ozonation conditions encountered at drinking water treatment plants. Little or no removal of these pesticides can be expected with ozone, or with other oxidants.

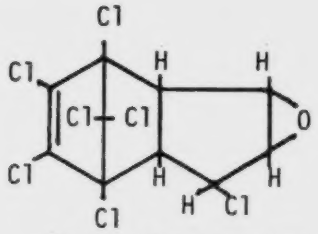
Malathion and parathion represent two unique cases of pesticides which are oxidized to destruction by ozonation, but which proceed through intermediates (their corresponding oxons) which are more toxic than are the starting thions (27).



Hoffman & Eichelsdörfer (28) showed that heptachlor is oxidized "quantitatively to destruction" with ozone but that heptachlorepoxide is stable to ozonation. This raises the question as to whether ozonation of heptachlor produces heptachlorepoxide, which itself is a very toxic material.



heptachlor



heptachlor epoxide

Thus it is incumbent upon a water supply system to identify the specific pesticides with which it must cope, then to ascertain the most effective method of removing them. If ozonation is a part of the water treatment process, certain pesticides can be removed effectively, but others will require a different treatment sequence.

2.10 Suspended Solids Removal (Turbidity)

Turbidity is caused by suspended solids, which are small, colloidal sized particles having surfaces which are highly charged. The strength of these surface charges, in fact, keeps the particles in suspension because of the repulsive surface forces coupled with the small particle sizes. Such colloidal particles normally pass through filters and are not retained.

In some instances addition of a strong oxidant, such as ozone, will change the nature and/or extent of these surface charges, thus allowing the charged particles to agglomerate and be more readily removed by subsequent filtration. If ferrous iron ions are present, ozonation will oxidize these to the ferric state, as discussed earlier.

As these trivalent ions hydrolyze and agglomerate, they interact with the surfaces of suspended solids, flocculating them and allowing them to be removed from suspension by filtration.

The use of ozonation alone can accomplish flocculation without the addition of soluble ions which remain in solution when chemical flocculants are used. A unique example of the use of ozone to reduce suspended solids is the recently commissioned Chino Basin sewage treatment plant, near Los Angeles, California in the United States. This secondary treatment plant is required to discharge an effluent which is very low in suspended solids and in total dissolved solids, because the water table in the area is very close to the surface. Simple filtration does not lower the suspended solids content sufficiently.

Were it not for the stringent TDS requirement, Chino Basin could treat its secondary effluent with alum or other standard chemical flocculating agents. However, such treatment in this case would require an additional step of removing the soluble chemicals after flocculation, coagulation and filtration. The cost of such multiple treatment is high and the process chosen was the single step of ozonation. An ozone dose of 10 mg/l provides the required coagulation of suspended solids so as to allow their ready removal by filtration. This 3 mgd plant went on stream in early 1978 and the process is operating satisfactorily (29).

2.11 Microflocculation

As discussed earlier, during oxidation of dissolved organic materials with ozone, oxygen is introduced into many of the carbonaceous sites in the molecules. Carboxylic acids, aldehydes, ketones and alcohols are produced, all of which are more highly polar than are the non-ozonized compounds. These polar compounds are capable of hydrogen bonding, which effectively increases their apparent molecular weights. In addition, the simultaneous presence of polyvalent metallic cations, such as iron and aluminum, with these polar organic groupings leads to flocculation of the oxidized organics. Therefore the ozonation of clear waters containing dissolved organic compounds can lead to an increase in turbidity. This process has been termed "microflocculation" by water chemists, and has been amply described in the preceding paper by Dr. Maier.

It is because of microflocculation that many water treatment plants insist upon following ozonation with a filtration step. The plant at Langenau, Germany, follows ozonation with a second addition of ferrous iron compounds to increase the rate of microflocculation, and produces a very clear water after subsequent filtration.

2.12 Ozone Pretreatment for Biological Processing

It has been pointed out in many examples given above that the partial oxidation of organic compounds with ozone renders them biologically degradable at a faster rate than before oxidation. This fact leads to the conclusion that if raw waters to be ozonized (or treated with any other oxidant) contain high amounts of dissolved organic carbon and those carbonaceous compounds are not readily removed by flocculation and are not readily oxidized to CO_2 and water by ozone, that ozonation will produce an aqueous medium high in dissolved oxygen and containing dissolved organic compounds which are more readily assimilated by biological organisms. This reasoning has led to the concept of incorporating biological treatment steps following ozonation. Since ozonized aqueous media are conducive to the development of aerobic bacteria, not only can the carbonaceous compounds be expected to be degraded biologically, but ammonia also can be expected to be converted to nitrate by biological nitrification processes.

Biological processes promoted by preoxidation (or by preaeration or preoxygenation in certain instances) can be incorporated into the water treatment process by addition of sand or anthracite filters and/or granular activated carbon filters. It has been known for many years that slow sand filters and activated carbon units contain high degrees of biological activity. Following ozonation with sand or anthracite filtration (to remove flocculated materials), then with GAC filtration has been incorporated into the Rouen-la-Chapelle plant in France and into the Dohne plant at Mülheim, Germany, specifically to remove ammonia biologically as well as dissolved organics. This technique thereby avoids (Rouen) or eliminates (Dohne) the need for breakpoint chlorination, with its attendent production of halogenated organic compounds which should be removed later in the treatment. The process has been termed Biological Activated Carbon by Rice et al. (30), and is being studied at many water treatment plants.

One of the promising secondary benefits of biological activated carbon is the greatly extended useful life of the GAC filter media because of the bacterial activity which is promoted by preozonation (or preaeration or preoxygenation in certain instances). The Rouen plant has operated satisfactorily since January, 1976 without having to regenerate its 75 cm deep GAC beds. Later in this meeting, Dr. Jekel will describe the BAC process as employed at the Dohne plant, which has not had to regenerate its 4 m deep GAC columns since they were installed in November, 1977. Expectations at Dohne are for at least two years of GAC operational life before regeneration will be required.

2.13 To Make Water Blue

The unique property of making finished water blue is one of the primary reasons given for its use at Langenau, Germany. This plant is located near the Danube River in southern Germany, and processes mostly groundwater. During dry seasons, however, Danube River water also is treated by a series of physical chemical processes, including two ozonation steps. Preozonation is employed for suspended solids removal and to dispose of off-gases from the primary ozonation step (for organics oxidation and microflocculation). The ozonation process is controlled partly by the shade of blue color which is imparted to the finished water. When the water is not sufficiently blue, more ozone is added.

3. Multiple Applications of Ozone

It is important to recognize that even though ozonation might be installed for a single purpose, say iron and manganese oxidation, many other benefits can be derived from its use. For example, at Rouen, Dohne, Wuppertal and Langenau, preozonation (sometimes with high-speed turbine contactors) aids in the flocculation process. Postozonation at Rouen is for disinfection while the preozonation is for manganese oxidation, organics oxidation and preparing the following sand and granular activated carbon beds for biological conversion of ammonia and removal of dissolved organics.

At the three Düsseldorf plants (Flehe, Holthausen and Am Staad), Duisburg and Wuppertal, ozone's primary function is iron and manganese oxidation. At the same time organics are oxidized and disinfection is obtained.

If ozone is applied for, say, color removal, near the end of the treatment process, a significant amount of disinfection also will be obtained. The conjunctive use of contactor off-gases from the primary ozone contacting chambers can be effective in such multiple ozonation treatment processes. These off-gases (which contain as much as 5 to 10 % of ozone)sometimes can be recycled economically to an early stage treatment step (as at Rouen, Mülheim and Langenau). Alternatively, the ozone in these off-gases either must be destroyed (thermally, catalytically, by passing through moist granular activated carbon) or diluted with air before being discharged to the atmosphere. If the volumes of contactor off-gases are not large, recycling them to an early stage oxidation step in the total water treatment process can be cost-effective.

4. Summary

Early application of ozonation in drinking water treatment was primarily in France for bacterial disinfection. In the late 1960s, French scientists defined the ozone contacting time and dosages required for viral inactivation, and France since has adopted an ozonation treatment standard for this purpose. Viral inactivation can be achieved if a residual of 0.4 mg/l of dissolved ozone can be measured at least 4 minutes after the initial ozone demand of the water has been satisfied.

Many other applications for ozone have evolved since ozonation was installed in Nice, France (1906), most of which are based upon the high oxidizing power of the gas. In Table 4 are listed the results of the PTI questionnaire survey of plants known to be using ozone in the various countries of the world where ozone is being used to significant extents.

In Figure 1 is shown a "conventional" drinking water treatment process involving coagulation, sedimentation, filtration and disinfection. The known uses for ozonation are included at the various points in this conventional process. Note that ozone is used at different locations in the drinking water treatment process, depending upon the purpose or purposes for which it is being used.

It is important to recognize that ozonation of dissolved organic materials will rarely proceed to completion, e.g. to produce CO_2 and water. In most cases two effects will be noted after ozonation of dissolved organic materials:

1) Dissolved organics will be converted to more highly oxygenated materials which can and do flocculate, resulting in an increase of turbidity. In these instances, ozonation usually is followed by a filtration step.

2) Dissolved organics will be converted to more highly oxygenated materials which are more readily biologically assimilable. Therefore, the higher the residual DOC after ozonation, the greater will be the chances for bacterial and slime growths in distribution systems, if additional disinfectants (such as chlorine, chlorine dioxide and chloramine) are not added after ozonation. Biological treatment processes after ozonation have been incorporated successfully into a few plants, and the concept is being studied in many more plants.

TABLE 4 Uses of ozonation by country responding to PTI questionnaires

Country	No. of Plants Using O_3	Question-naires Returned	Ozonation Used For						
			Bacterial Disinfection[(a)]	Viral Inactivation	Fe/Mn	T/O	Color Removal	Organics Oxidation	Turbidity
Great Britain	18	6	2 (0)	1	2	1	6	-	-
Belgium	9	1	(0)	1	-	1	1	1	-
The Netherlands	12	7	2 (1)	2	Fe-1	Taste 6 Odor 4	6	3	1
Austria	42	5	5 (4^b)	2	-	-	1	1	-
Switzerland	150	9	6 (1)	5	-	both-4 Taste 1 Odor 1	2	3	-
Germany	136	31	27 (10)	8	8-both Fe-1 Mn-1	both-11 + Taste-5	5	16	6
France	593	64	60 (28)	37	5-both Fe-2 Mn-1	both-31 Taste-5 Odor- 1	21	23	9
Canada	20	18	13 (3)	9	-	both-15 taste-3	3	4 (phenols-2)	-
USA	5	-	1 (1)	-	-	4	-	-	-

(a) No. of plants known to be using O_3 as terminal step or sole disinfectant

(b) More Austrian plants known to be using O_3 as terminal step (Dobias & Starz, 1977).

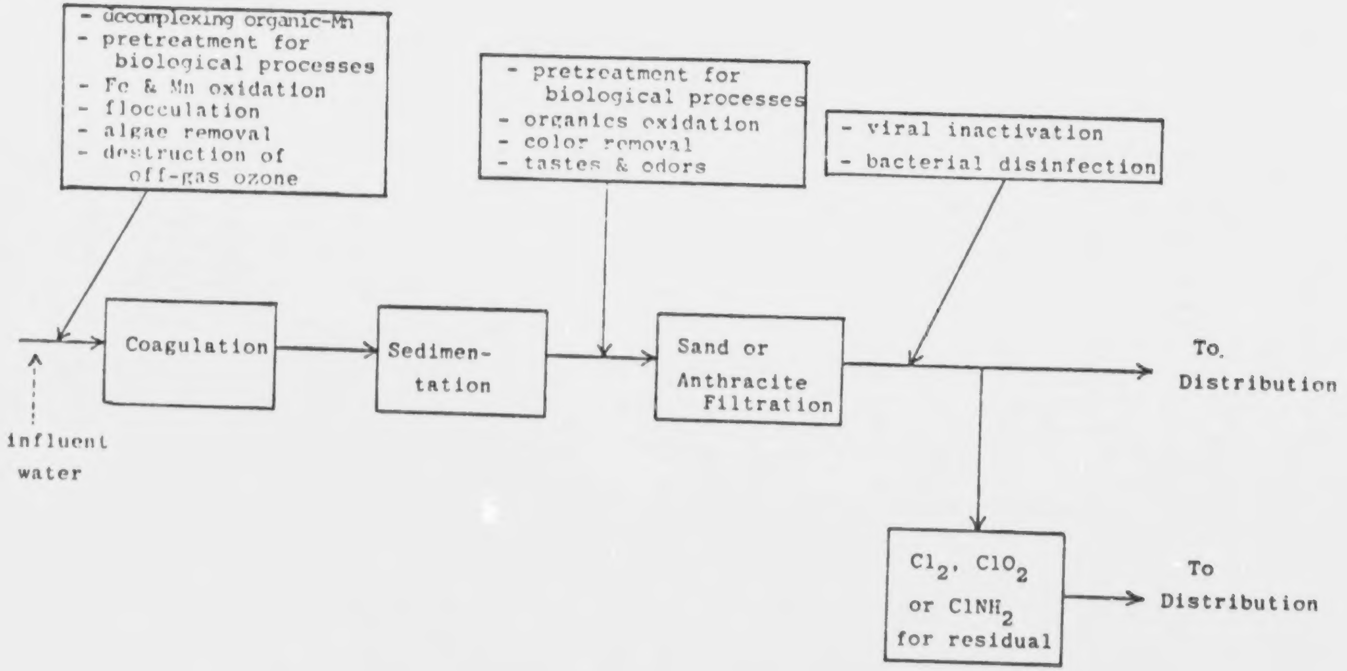


Fig. 1 Typical points of application of ozone in drinking water processes

TABLE 5 Major advantages and disadvantages of ozone

Advantages	Disadvantages
Powerful Oxidant	Non-Selective Oxidant
Powerful disinfectant and virucide over wide temperature and pH range	Leaves no residual for protection of network
Air preparation, ozone generation and contacting systems are easily automated -- but can be controlled manually	Gas/liquid contacting is not a general practice at water treatment plant
Generated on-site as needed -- operating costs 2-4 U.S. ¢/1,000 gallons	Capital costs for generation and contacting are relatively high
Safe -- shutting off electricity ceases O_3 generation	
Converts many non-biologically degradable organics to oxidation products which are biodegradable	will rarely oxidize all organics to CO_2 + water. Presence of Biodegradable Organics requires subsequent biological treatment and/or residual disinfectant, but at lower levels
Does not produce halogenated organics	Does not oxidize highly halogenated organics
Reduces amount of residual disinfectant required for network	
Adds dissolved oxygen to water	
Does not react with ammonia below pH=9	
Does not increase total dissolved solids	

In addition, it is also clear that because the capital costs for ozonation installations are high and because ozone reacts with a wide variety of materials, ozone should not be used to perform water treatment tasks that other techniques can do as well (or better) but at lower cost. For example, since suspended solids are easily removed by chemical coagulation, this process and filtration should precede ozonation for most other purposes.

The major advantages and disadvantages of ozone in treating drinking water are listed in Table 5.

(1) RIDEAL, E.K.
Ozone
Constable & Co. Ltd., London, England (1920)

(2) VOSMAER, A.
Ozone, Its Manufacture, Properties and Uses
D. van Nostrand Co., New York (1916)

(3) MILLER, G.W., RICE, R.G., ROBSON, C.M., SCULLIN, R.
WOLF, H., KÜHN, W.
An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Water Supplies
EPA Report No. 600/2-78-147. U.S. Environmental Protection Agency, Cincinnati, Ohio (1978)

(4) BARTUSKA, J.F.
Ozonation at Whiting, Indiana
J. AWWA 33 (1941), 11, 2035-2050

(5) BARTUSKA, J.F.
Ozonation at Whiting (Indiana): 26 Years Later
Public Works, August (1967)

(6) HARRIS, W.
Ozone Disinfection of the Strasburg, Pennsylvania, Water Supply System
Proc. First Internat. Symp. on Ozone for Water and Wastewater Treatment. R.G. Rice & M.E. Browning (editors)
Internat. Ozone Inst., Cleveland, Ohio (1975), 186-193

(7) LACY, W., RICE, R.G.
The Current Status of Ozone Treatment Technology in the United States
Presented at Special Seminar on Water Supply, Internat. Bank for Reconstruction & Development, Washington, D.C. Jan 11, 1978. See also Wasser Berlin 1977, AMK Berlin Germany/Internat. Ozone Inst., Cleveland, Ohio, 1978

(8) GUINVARC'H, P.
Three Years of Ozone Sterilization of Water in Paris
Ozone Chem. & Technol., Adv. in Chem. Series, 21, Am. Chem. Soc., Washington, D.C. (1959), 416-429

(9) O'DONOVAN, D.C.
Treatment with Ozone
J. AWWA 57 (1965), 9, 1167-1192

(10) HARDEN, C.H.
The Boxley Works of the Maidstone Waterworks Company
Trans. Inst. Water Engrs. 48 (1943), 152

(11) COIN, L., HANNOUN, C., GOMELLA, C.
Inactivation of Poliomyelitis Virus by Ozone in the Presence of Water
la Presse Med. 72 (1964), 37, 2153-2156

(12) COIN, L., GOMELLA, C., HANNOUN, C., TRIMOREAU, J.C.
Ozone Inactivation of Poliomyelitis Virus in Water
la Presse Med. 75, 38, 1883-1884

(13) SCHULHOF, P.
Private Communication, 1977

(14) HOIGNE, J.
Private Communication, 1978

(15) MASSCHELEIN, W.
Chlorine Dioxide (Chemistry and Environmental Impact of Oxychlorine Compounds)
Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1978)

(16) SCHACK, C.J., CHRISTE, K.O.
Inorg. Chem. 13 (1974), 378

(17) KÖLLE, W.
Problem der gemeinsamen Anwendung verschiedener Oxydationsmittel bei der Wasseraufbereitung
Vom Wasser 35 (1968), 367-381

(18) RICE, R.G., MILLER, G.W.
Reaction Products of Organic Materials With Ozone and With Chlorine Dioxide in Water
Presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Nov. 1977. Internat. Ozone Inst. Cleveland, Ohio (1977)

(19) EISENHAUER, H.R.
The Ozonization of Phenolic Wastes
J. Water Poll. Control Fed. 40 (1968), 11, 1887-1899

(20) EISENHAUER, H.R.
Dephenolization by Ozonolysis
Water Research 5 (1971), 467-472

(21) HILLIS, M.R.
The Treatment of Phenolic Wastes by Ozone
Presented at Third Internat. Symp. on Ozone Technol., Paris, May 1977. Internat. Ozone Inst., Cleveland, Ohio (1977)

(22) GILBERT, E.
Ozonolysis of Chlorophenols and Maleic Acid in Aqueous Solution"
Proc. Sec. Internat. Symp. on Ozone Technology
R.G. Rice, P. Pichet & M.A. Vincent (editors), Internat. Ozone Inst., Cleveland, Ohio (1976), 253-261

(23) GILBERT, E.
Chemical Reactions Upon Ozonization
Presented at Internat. Symp. on Ozone and Water, Wasser Berlin 1977, AMK Berlin/Internat. Ozone Inst., Cleveland, Ohio (1977)

(24) GILBERT, E.
Reactions of Ozone with Organic Compounds in Dilute Aqueous Solution: Identification of Their Oxidation Products
Ozone/Chlorine Dioxide Oxidation Products of Organic Materials. R.G. Rice & J.A. Cotruvo (editors), Internat. Ozone Inst., Cleveland, Ohio (1978), 227-242

(25) HOIGNE, J., BADER, H.
Ozonation of Water: Selectivity and Rate of Oxidation of Solutes
Presented at Third Internat. Symp. on Ozone Technol. Paris, May 1977. Internat. Ozone Inst., Cleveland, Ohio (1977)

(26) HOIGNE J., BADER, H.
Rate Constants for Reactions of Ozone With Organic Pollutants and Ammonia in Water
Presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov. 1977., Internat. Ozone Inst., Cleveland, Ohio (1977)

(27) RICHARD, Y., BRENER, L.
Organic Materials Produced Upon Ozonization of Water
Ozone/Chlorine Dioxide Oxidation Products of Org. Materials
Internat. Ozone Inst., Cleveland, Ohio (1978), 169-188

(28) HOFFMAN, J., EICHELSDÖRFER, D.
Zur Ozoneinwirkung auf Pestizide der Chlorkohlenwasserstoffgruppe im Wasser
Vom Wasser 38 (1971), 197-206

(29) NOWAK, T., TATE, C.H., MOUTES, J.G., STONE, B.G., TRUSSELL, R.R.
Full-Scale Tertiary Wastewater Treatment Plant
Presented at Ozone Technol. Symp., Los Angeles, May 1977
Internat. Ozone Inst., Cleveland, Ohio (1978)

(30) RICE, R.G., MILLER, G.W., ROBSON, C.M., KÜHN, W.
Biological Activated Carbon
Carbon Adsorption, P. Cheremisinoff & F. Ellerbusch (editors), Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1978)

THE USE OF OZONE IN THE TREATMENT OF DRINKING WATER

J. Chedal

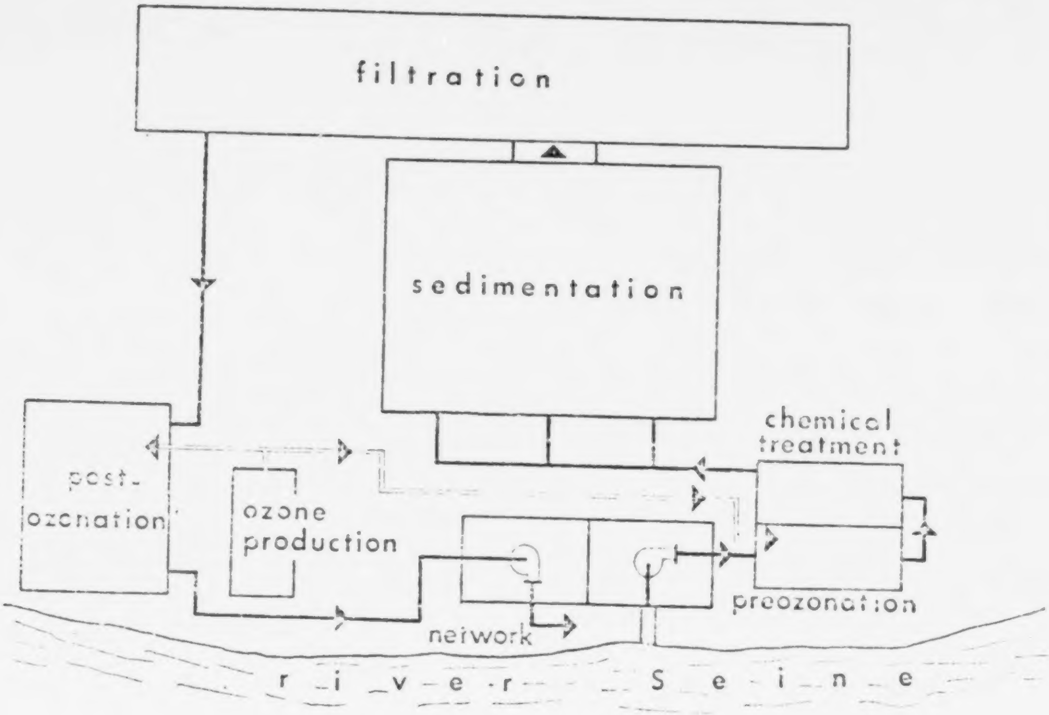
I should like to comment on the present and future use of ozone in the waterworks supplying the suburbs of Paris with drinking water by the treatment of surface water.

For 10 years ozone has been used in the after-treatment after a physical and chemical clarification. The main function of this treatment is to guarantee a viricidal final sterility. This aim is fulfilled by maintaining a residual ozone level of 0.4 g/m^3 in the water for 10 min. To achieve this, according to the provisions described by R. Rice, the ozone is added in consecutive chambers.

When the experiments which I described yesterday are completed we shall convert this chemical plant into a biological plant and so make use of ozone in the preliminary treatment of the raw water before each chemical treatment. This new treatment process makes it possible to achieve two different aims:

1. The preliminary break-point treatment with chlorine is avoided. In the new process the ammonia is eliminated biologically during the clarification. The advantage of this process is that the formation of haloforms during the preliminary treatment is prevented.

2. During the clarification phase the removal of organic substances is increased. This reduction in their content largely affects the precursors. Consequently, the final chlorination for protection of the network gives rise to only minimal haloform formation.



The additional removal of organic substances achieved by this method of ozonization is certainly partly due to the coagulating action of ozonization. The various aspects of this phenomenon have just been presented by Dr. Maier.

To put this new approach into practice the measures shown in the adjoining scheme were taken in the largest waterworks supplying drinking water to the Paris suburbs (capacity 900,000 m^3/day). The structures for the preliminary ozonization comprise a container for preliminary chemical treatment, which is currently under construction.

The experiments have shown that a preliminary ozonization with 1 ppm makes possible an equally large reduction of the ozone dose in the after-treatment.

Accordingly, no additional ozonization equipment need be installed. The present ozone generator is adequate for the after-ozonization plants and for the preliminary ozonization.

The development I have just described shows how careful one must be in the planning of a water-treatment works. It is always desirable to make provisions for the incorporation of additional processes in a treatment plant.

As regards the ozone, it is best if its generation and application are kept separate. To enhance the quality of the treatment it may be advisable to apply the ozone at several points in the treatment line, particularly in the preliminary ozonization as in the present case.

SYNERGISTIC EFFECT OF OZONE AND CHLORINE ON BACTERIA AND VIRUSES IN SECONDARY WASTEWATER EFFLUENTS

Y. Kott

Synergistic effects are prevalent in nature and are mostly studied as factors of growth inhibition; synergism was also observed when gamma radiation and heat were used together in order to decrease the number of microorganisms found in wastewater sludge. The current study, supported by joint German/Israeli Research Projects BMFT and NCRD Project No. 013-714, was undertaken with a view to finding whether or not simultaneous application of chlorine and ozone to secondary wastewater would involve in a synergistic effect. Various studies have shown that ozone, chlorine and other disinfectants reduce microorganism counts in secondary wastewater effluents. In the present study, chlorine at concentrations of 5-30 mg/l, applied to a continuous flow sample in a column, showed reduction of coliform at range of bacteria 10^6/100 ml by one order of magnitude up to five, that is 0-2 bacteria in 100 ml. Poliovirus count (attenuated strain) at range of 10^4/5 liter samples decreased by up to two orders of magnitude at the most.

When ozone was applied at concentrations of 10-25 mg/l to secondary wastewater under the same experimental conditions the count of coliform bacteria decreased from 10^5/100 ml to 10^4/100 ml which is one order of magnitude, and that of enteroviruses from 10^4/5 liters to 30 which is three orders of magnitude. Different concentrations of these oxidation chemicals applied for different contact times showed that chlorine has a much higher kill efficiency for bacteria than for viruses, while the reverse effect was observed with ozone. In addition *Salmonella typhymurium* a bacteria representing the pathogens, and T_2 bacteriophage representing other viruses were examined. The results showed that ozone caused an 80 percent decrease for the bacteria and a 95 percent decrease for Polio I attenuated viruse particles at equivalent experimental conditions. When the synergistic effect of chlorine and ozone was studied, the chemicals were applied separately, together and in sequence, all on the same experimental set-up.

Definite synergistic effect was observed with a better kill effect on bacteria and viruses. The order of sequential application made no difference. Further study on the synergistic effect is under way for economic evaluation.

EXAMPLE OF UV OZONE CONTROL - ELIMINATION OF RESIDUAL OZONE

J. Valenta

The equipment and apparatus available commercially at the present time enable continuous monitoring of the ozone concentrations both in air-ozone or oxygen-ozone mixtures and in ozonized water.

As an example of suitable ozone monitoring I should like to describe briefly - from our own practical experience - the continuous monitoring of the residual ozone content in the outgoing air of a newly installed ozone eliminator in the lake waterworks at Lengg.

Here we were able to detect at times certain ozone emissions, lasting only a short time, particularly during the backwash of the activated carbon filters. The situation is illustrated in Fig. 1.

It was therefore decided to supplement the original thermal ozone elimination by a catalytic decomposition unit, the earlier plant additionally assuming the function of preheating the exhaust gas upstream of the catalyst.

After the installation of the new elimination plant the performance was monitored with the aid of two continually running ozone detectors based on the principle of UV measurements. One instrument, with a 2 cm quartz cell,was placed at the entrance (position 3), the other, with a 50 cm long cell, was placed downstream of the catalyst (position 6). In addition, the residual ozone concentrations at seven other points along the air outlet were measured over a short period. A low-pressure mercury lamp serves as the light source in these instruments, providing light with almost 95% of the 254 nm wavelength.

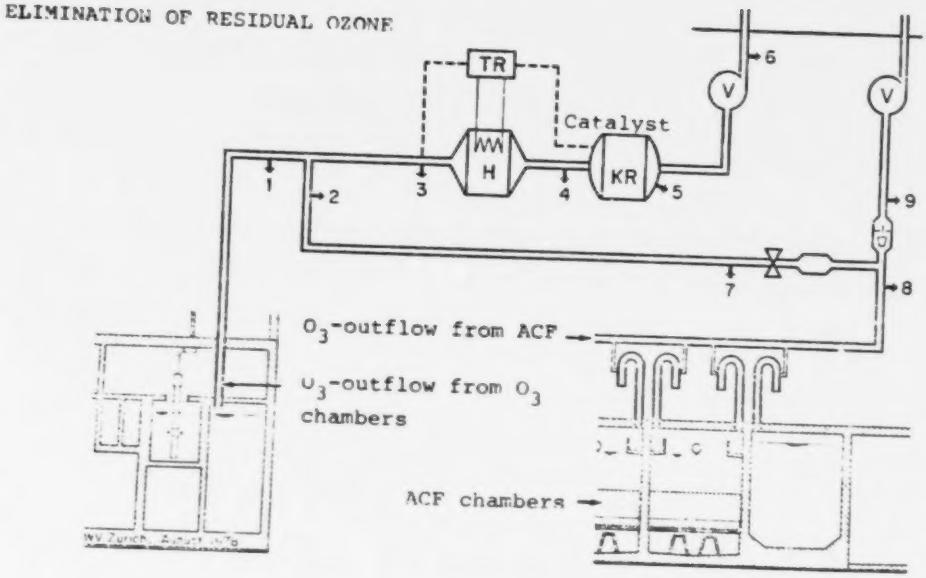

ELIMINATION OF RESIDUAL OZONE
TR
Catalyst
H
KR
V
V
1
2
3
4
5
6
7
8
9
O_3-outflow from ACF
O_3-outflow from O_3 chambers
ACF chambers

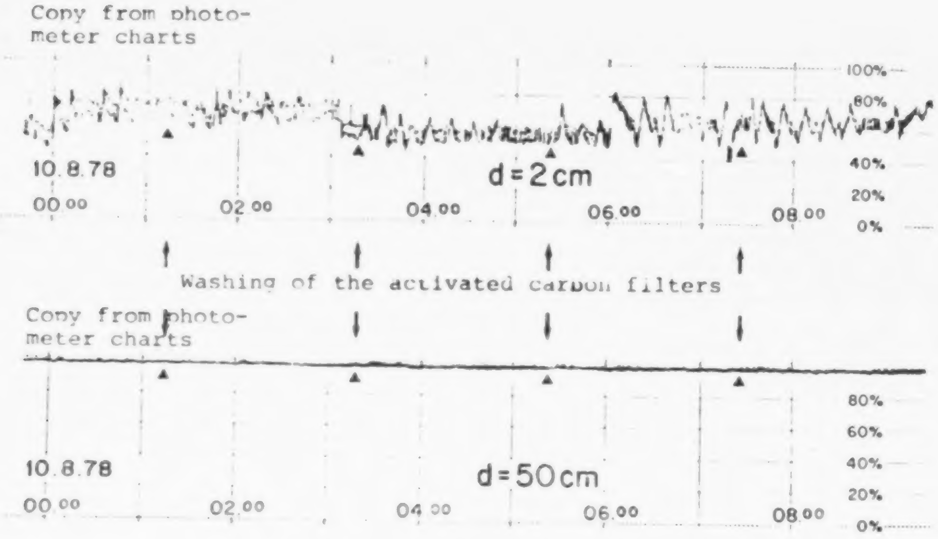
Fig. 1 Control of the catalytic elimination of residual ozone in the lake waterworks at Lengg

To obtain the desired flow-through velocity of the measured gas mixture, a small ozone-resistant membrane pump and a rotameter were connected at the second photometer (6).

The flow velocity was here practically a constant, between 0.6 and 0.8 l/min, in the course of several days.

Fig. 2 shows two recorder charts with the data evaluation before the elimination and after the catalytic decomposition. The activated carbon filter washes, during which an earlier elevated ozone concentration in the outgoing air could be detected, are also marked. At the input the ozone content was at the maximum 3 mgO_3/l, corresponding to about 1500 ppm of ozone, while after the eliminator 0.01 mg of ozone/l (5 ppm) was never exceeded. The large layer thickness in the second instrument makes it possible to determine ozone concentrations down to 0.01 mg O_3 per litre of outgoing air.

This figure demonstrates the very high performance of the catalytic elimination of ozone and at the same time the feasibility of using the UV method for this purpose.



WV Zurich, August 1978

Fig. 2 Recorder charts of the UV measurement of residual ozone

USE OF CHLORINE DIOXIDE FOR THE TREATMENT OF DRINKING WATER

W.J. Masschelein

1. INTRODUCTION

Though the bactericidal properties of chlorine dioxide have been known since the beginning of the century, the compound has only been used in the field of water treatment since the nineteen-fifties. It was when chlorine, which was in any case fairly cheap, had been found not to be entirely satisfactory when used on its own as a disinfecting agent, that other agents such as chlorine dioxide began to be used. Many large Water Boards, such as the Paris one (both city and suburban), the Düsseldorf Board, and many others adopted chlorine dioxide. The results obtained were and still are very satisfactory, notwithstanding certain reservations expressed by some users. Owing to conservatism and ignorance, frequent attempts were made to use facile pretexts to cast doubt upon the use of chlorine dioxide: instability of the reagent, handling risks, lack of a good method of analysis, especially for residual quantities, appearance of residual chlorite for which there was no reliable method of analysis.

It was during this period, and more precisely in 1968, that the use of chlorine dioxide was adopted by the Compagnie Intercommunale Bruxelloise des Eaux. In its time, this decision required two years of preliminary research, both documentary and laboratory investigation with technical development. At present, as we know, the accumulation of knowledge concerning the formation of organochlorine compounds has renewed the interest in chlorine dioxide, as indeed in other possibilities of water treatment.

Since the time allotted for this paper does not enable me to develop exhaustively the prospects and the limitations of chlorine dioxide, I shall refer to earlier monographs (1,2). All the same, I shall try to highlight their most important aspects, and above all the criticisms alluded to above.

2. PRACTICAL SYNTHESIS OF CHLORINE DIOXIDE

Chlorine dioxide is a gas that must be prepared in situ where it is to be used. The synthesis reactions used in treatment stations are as follows:

$$2\ NaClO_2 + Cl_2 = 2\ NaCl + 2\ ClO_2$$

and

$$5\ NaClO_2 + 4\ HCl = 4\ ClO_2 + 5\ NaCl + 2\ H_2O$$

The oxidation of chlorite by persulphate is in most cases limited to swimming pools:

$$2\ ClO_2^- + S_2O_8^= = 2\ ClO_2 + 2\ SO_4^=$$

Synthesis starting from chlorates (1,2) is hardly ever used. It is more suitable for production capacities much larger than those that suffice for water treatment.

2.1. In the synthesis of chlorine dioxide from chlorite and chlorine, a minimum concentration of chlorine is required to enable sufficiently rapid formation of the chlorine dioxide without any concomitant dismutation reaction that would give chlorate according to the probable mechanism:

$$6\ ClO_2 + 3\ H_2O = 5\ HClO_3 + HCl$$

In fact, the acidity of the water due to the chlorine serves mainly to neutralize the alkalinity introduced by the stabilized chlorite. At initial chlorine concentrations of the order of 0.4 to 0.5 $kg.m^{-3}$ one must work with approximately equal weights of chlorine and sodium chlorite, namely an amount of chlorine equal to 200 to 250% of the stoichiometric amount. With 1 to 1.5 kg of chlorine per m^3 in the initial solution the reaction attains a 90% yield, the final pH of the soluiton being between 4 and 5. At higher chlorine concentrations, up to 3 $g.\ell^{-1}$, a stoichiometric mixture with sodium chlorite gives a yield greater than 95%, at a final pH lying between 5 and 6. This solution also contains up to 6 g of ClO_2 per litre.

If one operates at these concentrations, the equilibrium vapour pressure of the dioxide gives rise to a concentration, in the gaseous phase, of 6 vol-% at 15°C and 10 vol-% at 30°C. After the reaction phase it is thus necessary to dilute the solution if the reagent is to be preserved for a certain time before being injected into the water to be treated. This operation is advantageous mainly in that it permits metering in proportion to the flow rate of the water being treated. The dilution will keep the pH between 5 and 7.5, so that both acidic and alkaline dismutations will be avoided. The final concentration attained is between 0.5 and 1 g of ClO_2 per litre.

2.2. For the surplus (see Fig. 1) the following safety measures should be taken:

- automatic cut-off of chlorite in the event of insufficient chlorine;
- cut-off of gaseous chlorine in the event of insufficient water

- provision of a dilution zone within the reactor;
- ventilation of any storage tanks, which will also avoid any build-up of pressure inside them;
- safety vents on the pipelines leading the gases towards the ClO_2 elimination plant: graphite plates for the ClO_2, or sodium hydroxide exchanger, depending on the capacity of the installation;
- all the joints and connections of the reactor and the plant must be made using flame-proof materials and installation methods;
- free ventilation, or preferably an extractor fan, for the chlorite storage hopper.

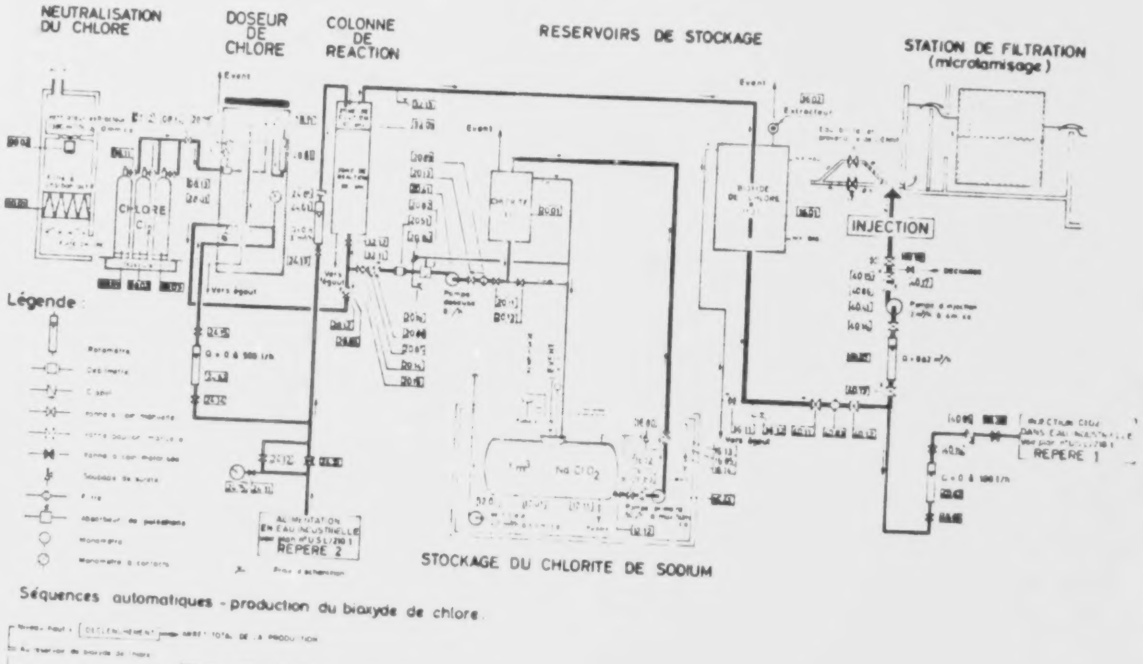

NEUTRALISATION DU CHLORE
DOSEUR DE CHLORE
COLONNE DE REACTION
RESERVOIRS DE STOCKAGE
STATION DE FILTRATION (microtamisage)
Event
Extracteur
CHLORE
INJECTION
Légende
1 m³
NaClO2
ALIMENTATION EN EAU INDUSTRIELLE
REPERE 2
REPERE 1
STOCKAGE DU CHLORITE DE SODIUM
Séquences automatiques - production du bioxyde de chlore

Fig. 1 Plant for the preparation of ClO_2 from $NaClO_2$ and Cl_2. Example: the Lienne station.

Reactors similar to the one illustrated here and capable of producing up to 7.5 kg/h of ClO_2 have been operating for several years at the Tailfer station.

2.3. The direct reaction involving stoichiometric proportions of chlorite and hydrochloric acid, and producing chlorine dioxide at concentrations of 0.5 to 2 g.ℓ$^{-1}$, only proceeds with a yield of 60 to 80%. Various secondary reactions result in the formation of chlorine:

$$5\ ClO_2^- + 5\ H^+ = 3\ ClO_3^- + Cl_2 + 3\ H^+ + H_2O$$
$$4\ ClO_2^- + 4\ H^+ = 2\ Cl_2 + 3\ O_2 + 2\ H_2O$$

Moreover, the chlorous acid appearing as an intermediate in the reaction can undergo dismutation according to:

$$4\ HClO_2 = 2\ ClO_2 + HClO_3 + HCl + H_2O$$

Yields of up to 100% for ClO_2 formation, i.e. the production of four moles of dioxide from five moles of chlorite, may be attained provided that the reagents $NaClO_2$ and HCl are mixed in equal weights, in the form of solutions with concentrations of 7.5 wt-% of $NaClO_2$ and 9 wt-% of HCl. These conditions imply a final pH of less than 0.5.

This technique means that the commercial chlorite, at 24-25 wt-% (300 kg.m^{-3}) must be diluted, an operation best performed with softened or demineralized water so as to avoid the precipitation of calcium carbonate and calcium silicate (with magnesium oxide) in the solution used. To avoid these difficulties, we at C.I.B.E. have developed a high-concentration process based upon the direct use of commercial 300 kg.m^{-3} sodium chlorite and acid diluted 1 + 6. Under these conditions the reaction is complete within about 10 min and the dioxide is produced at a concentration of some 25-30 g.ℓ$^{-1}$.

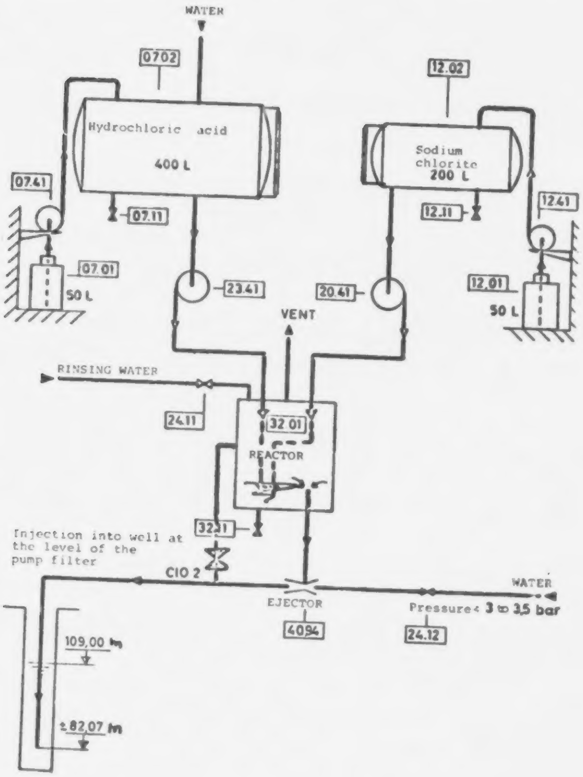


Fig. 2 General layout of this type of plant

The yield depends on the design of the zone in which the reagents are mixed within the reactor. A contact enclosure in the shape of an inverted cone with tangential inlets for the reagents gives excellent results. The reactor can be reliably brought into operation by maintaining a reduced pressure with an ejector that draws off both dissolved and gaseous dioxide. For safe operation it is essential to provide automatic shut-down in the event of an insufficiency of the dilution water, by means of the ejector or by discontinuing the reduced pressure. The other precautions, such as ventilating the pipelines, fire-proofing safeguards for the chlorite storage, etc. are similar to those for the chlorite + chlorine reactors.

2.4. Preparation in the laboratory

If 1.5 to 2 moles of acetic anhydride per $NaClO_2$ are made to react with an aqueous solution of sodium chlorite, a pure solution of chlorine dioxide is obtained with a yield of 50% (3). The remainder of the chlorite is transformed into chlorate, together with traces of chlorides, while the acetic anhydride is converted into the acid and acetate.

Such as it is, this solution is satisfactory for most applications in the laboratory or on a small scale, in which the impurities mentioned above do not interfere. If the dioxide needs to be purified, this can be done by scrubbing with air and redissolution. This operation is performed in the dark to prevent any dismutation (4).

3. METHODS OF ANALYSIS

3.1. Iodometry is still the best method of determination, both for the chlorine dioxide and the chlorite, provided that other oxidizing agents that can oxidize iodide to iodine are absent.

At pH 7 the reaction is:

$$2\ ClO_2 + 2\ I^- = I_2 + 2\ ClO_2^-$$

At pH 2 the chlorite reacts according to:

$$ClO_2^- + 4\ I^- + 4\ H^+ = 2\ I_2 + 2\ H_2O + Cl^-$$

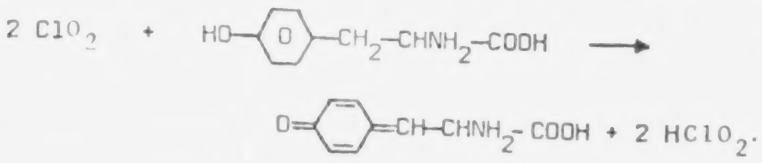
Under the practical treatment conditions the chlorine is the major source of interference. Because of this, the iodometric method is mainly suitable for calibration.

3.2. The simultaneous determination of several oxidants, such as chlorine dioxide, chlorite, and chlorine, often entails an alkaline dismutation phase of the dioxide into chlorite and chlorate:

$$2\ ClO_2 + 2\ NaOH = NaClO_2 + NaClO_3 + H_2O$$

In fact, we have observed that the dioxide is notoriously unstable in the presence of other oxidizing agents (1, p.40; 2). Cross dismutations occur. Analytical results implying the above dismutation must be considered suspect in the case of solutions containing oxidizing agents other than chlorine dioxide. The same is true of the colorimetric methods based on o-toluidine or DPD. In fact, we suggest that the results obtained in the presence of mixtures should be considered as purely arithmetical.

3.3. As an alternative to the iodometric method, the colorimetric determination of chlorine dioxide by oxidation of tyrosine to dopaquinone (5) constitutes a method of analysis for concentrated solutions.



At pH 4.5 the reaction is selective and the determination is effected by measuring the absorption at 490 or 355 nm. The interference due to chlorine is not very significant for Cl_2/ClO_2 ratios smaller than 2. If necessary, it can be eliminated by the addition of ethylamine or malonic acid. The sensitivity of the method is 0.2 g $ClO_2.m^{-3}$.

3.4. Acid Chrome Violet K (ACVK), i.e. 1,5-bis-(4-methylphenylamino-2-sodium sulphonate)-9,10-anthraquinone (colour index number CI 61,710), makes possible a selective determination of chlorine dioxide in residual concentrations in water. This method involves (6) decolouration of the reagent in an ammoniacal medium buffered to pH 8.1 to 8.4. This is measured at a wavelength of 550 nm (a compromise for the hypsochromic shift of the absorption band).

With the familiar spectrophotometric techniques the sensitivity and the precision are 0.04 g $ClO_2.m^{-3}$. A value of 0.02 g $ClO_2.m^{-3}$ may be attained by microcell techniques and by thermostatting the test solutions. The method can also be used for the determination of ozone (7). Reference should be made to that publication for certain operating precautions additional to those described in the original work. In practice, interference from ozone need not be feared since, like the chlorite in solution, the chlorine dioxide is oxidized to chlorate under the action of ozone.

The use of the ACVK method has been proposed for the determination of chlorine dioxide in applications relating to the treatment of waste waters (8). Since the method is colorimetric, there is a possibility of interferences in this case, but investigation has established a rigorous parallelism between the results of the colorimetric method and the results obtained by analysis of the nuclear paramagnetism. This latter absolute technique is difficult to apply in practice, but it has been used to confirm the specificity and the reliability of the ACVK method.

3.5. The formation of residual chlorite by reduction of chlorine dioxide is an awkward feature in the application of chlorine dioxide to the treatment of drinking water. It makes it necessary to control the residual chlorite in the water, especially since this compound can be toxic when its concentration is too high.

The only specific and sufficiently sensitive method that we can suggest is based on a technique involving the differential plotting of polarograms obtained by means of pulsed currents.

The electrode reaction is based on the following over-all equation (9):

$$HClO_2 + 4\ e + 3\ H^+ = Cl^- + 2\ H_2O$$

We recommend the following specimen pre-treatment (10): adjust the pH to 4.4-4.5 with a buffer, so as to produce the final concentrations CH_3COONa 0.04 M, CH_3COOH 0.06 M, and $(NH_4)_2\ SO_4$ 0.01 M. If present, chlorine and chlorine dioxide are removed by bubbling nitrogen through the measuring cell. (If the presence of heavy metal ions in concentrations that may cause disturbances is suspected, the water should be passed through a strong cation-exchange resin).

The polarograms in the pulsed mode are recorded and, by difference, a linear relationship is obtained between the differential diffusion current and the concentration of dissolved chlorite. The sensitivity is 0.05 g $ClO_2^-.m^{-3}$ (10).

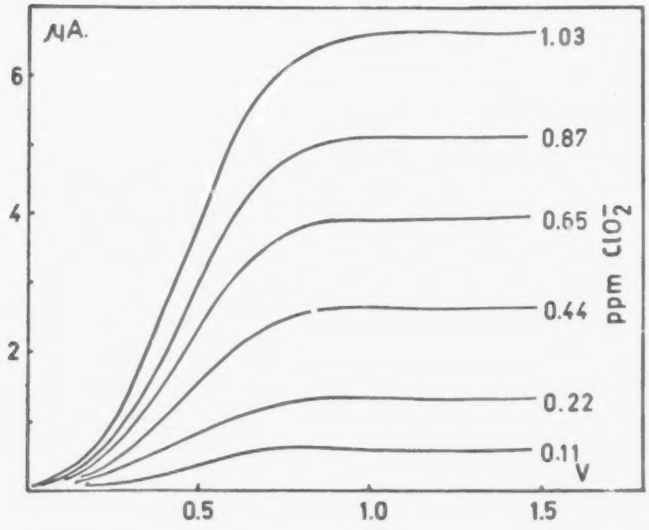


Fig. 3

Chlorite polarogram (graphical construktion by difference, in the pulsed mode)

3.6. The practical use of chlorine dioxide in the treatment of drinking water often entails continuous monitoring of the residual oxidants. In this connection we have developed an amperometric analyser for the iodine obtained when iodides are brought into contact with oxidizing agents.

The analyser is based on the galvanic couple Ag/Au which gives a zero residual diffusion current. A mixture containing 0.090 m^3 of acetic acid and 800 g of KI per m^3 is added to the water being analysed, so as to obtain a final pH of 5. Stabilization of the latter is based upon the buffering effect due to the bicarbonate present in the water.

The direct output current obtained using curved electrodes with an area of 3000 mm^2, separated by a distance of about 50 mm, and with a 1000 Ω resistance connected in series, is 12.5 $mA.Eq^{-1}.m^{-3}$. The chlorine, the chloramines, and the chlorine dioxide are shown up in accordance with their capacity to oxidize iodides at pH 5. Chlorites do not interfere. The sensitivity is of the order of 0.01 g $ClO_2.m^{-3}$ (11).

4. RISKS INHERENT IN THE USE OF ClO_2

4.1. In the gaseous state chlorine dioxide is spontaneously explosive at concentrations higher than 10 vol-% (12). The reaction is induced by any source of ignition. At 20°C, this concentration in the gaseous phase corresponds to a concentration of about 8 $g.\ell^{-1}$ of ClO_2 in solution. The acidification process thus generates a dangerous atmosphere. The maximum allowable concentration in working premises is 0.1 ppm by volume for an 8-h work shift per day, and 0.3 ppm for brief occupations. Chlorine dioxide is perceptible in the air at concentrations of 1.4 to 1.7%. At 4.5% it irritates the respiratory mucosae and produces severe headaches.

There is no cumulative effect in the event of repeated exposure (13).

4.2. In drinking water the maximum residual content that does not affect the taste or produce a disagreeable odour is of the order 0.4 to 0.5 g ClO_2 per m^3. This concentration is also lower than the maximum allowable concentration from the point of view of toxicity, since tests on rats have not shown any serological toxicity at doses as high as 5 $g.m^{-3}$ (14). In Belgium the maximum concentration of chlorine dioxide tolerated in water distributed through the public mains is 0.25 $g.m^{-3}$.

4.3. At least some of the dioxide used is likely to be transformed into chlorite by reaction with organic compounds. The chlorite is toxic and can cause methaemoglobinaemia. However, the LD_{50} of sodium chlorite for rats is 140 $mg.kg^{-1}$ On the extreme assumption that all of the dioxide could be transformed into chlorite, this value of LD_{50} corresponds to 105 mg $ClO_2.kg^{-1}$. Consequently, there seems to be no objection to the use of chlorine dioxide, in the usual amounts, on these grounds.

5. ADVANTAGES OF CHLORINE DIOXIDE TREATMENT

5.1. It has been found that the cost of post-disinfection with chlorine dioxide, compared to that of chlorine, is 1.2 to 1.7 times as high (15,16). However, the relative cost of treating raw water can change appreciably as a function of local parameters. Thus, ratios of 1/1 to 1/4 have been found (17). The raw water is treated at the Tailfer station of the Compagnie Intercommunale Bruxelloise des Eaux both with chlorine and the dioxide. The average amounts have been equal to 1.3 g $ClO_2.m^{-3}$ and 6 g $Cl_2.m^{-3}$, corresponding to a respective cost of 1 to 2.4 for the chlorine compared to the dioxide used.

5.2. The use of chlorine dioxide constitutes an alternative to prechlorination. One of its advantages is the smaller tendency to form organochlorine derivatives, bearing in mind the reactivity of organic derivatives with this oxidant (2). Moreover, chlorine dioxide forms few, if any, simple chlorinated hydrocarbons of the chloroform type (18). Another, often decisive, advantage consists in the fact that chlorine dioxide does not react with dissolved ammonia. Thus, it is not essential to use amounts greater than the critical point to obtain satisfactory disinfection. This point is also important for the treatment of swimming pools.

Like ozone, chlorine dioxide leads to micelle formation in the coagulation-flocculation pre-treatment. Because of this, the turbidity of swimming pool waters treated with chlorine dioxide is lower than that obtained by a comparable treatment with chlorine (19). Moreover, iron and manganese, which may be present in the reduced or complexed states, particularly in association with fulvic or humic acids, are oxidized and eliminated by subsequent precipitation.

One of the most important aspects of using chlorine dioxide for the pretreatment of river water is the competition between the oxidation reactions that produce chlorite and the dismutation into chlorate and chlorites. The respective reactions are:

$$ClO_2 + 1\ e^- = ClO_2^-$$

$$6\ ClO_2 + 3\ H_2O = 5\ HClO_3 + HCl$$

According to this scheme the ClO_2^-/ClO_3^- mass concentration ratio of 1 corresponds to a molar concentration ratio of 1.24. Thus, if the ClO_2^-/ClO_3^- mass ratio is observed to be 1, about 7.4 moles of initial dioxide will have reacted for each mole lost by dismutation.

This dismutation of chlorite is slow in the absence of light. The following reaction is of minor importance except in the event of intense insolation:

$$3\ ClO_2^- = 2\ ClO_3^- + Cl^-$$

Experience has given the following recommendations in relation to the practical use of chlorine dioxide for the treatment of raw water:

- A reaction time of 30 to 40 min is sufficient.
- The residual ClO_2 concentration after this time should not normally exceed 0.2 $g.m^{-3}$.
- The chlorite/chlorate mass ratio after this action should be between 1 and 2, corresponding to an effective degree of reaction of 83 to 91%. For a decantation tank open to the air, if the residual concentration of ClO_2 exceeds 0.2 $mg.\ell^{-1}$, the loss of ClO_2 by dismutation into chlorides and chlorates increases.

Moreover, the decomposition of chlorine dioxide by active carbon, as used in coagulation-flocculation, is appreciably less rapid than that of chlorine (20). Thus, it becomes possible to maintain a bactericidal activity in sludges containing flocculated carbon.

5.3. During post-chlorination, chlorine dioxide can maintain itself in clean water for up to 48 h. Thus, its bactericidal efficacy is guaranteed for a longer time than that of chlorine. The same conclusion is relevant to the persistence of a disinfecting action in swimming pools (21). The disinfecting action of chlorine dioxide is recognized to be at least equal to that of chlorine, and superior in the case of waters with a pH higher than neutral. In this connection we refer to our previous analysis to support this conclusion (2). It seems, in fact, that the diffusion of chlorine dioxide depends very little on pH compared to that of chlorine in its various forms in equilibrium. I shall not present here an exhaustive review of the bactericidal and disinfectant properties of chlorine dioxide, since this lies outside the scope of the present paper, and merely refer to previous reviews of the subject.

5.4. After the reaction a significant proportion of the chlorine dioxide is reduced to chlorite. It is thus interesting to examine the bactericidal or bacteriostatic properties of the chlorite ion, in relation to post-disinfection.

The disinfectant power of the chlorite ion is minor. Thus, the philosophy of post-disinfection with chlorine dioxide rests on the action of chlorine dioxide itself, which is a strong bactericide, followed by that of the chlorite, which is weakly bacteriostatic and weakly bactericidal. The chlorite, in its own right, is not used directly in disinfection. However, we have tried to determine its bactericidal and bacteriostatic effects.

5.5. The bactericidal effect upon enterobacteria is shown in Figs. 4 and 5.

In physiological water, type C coli were removed, during the experiments, in accordance with Chick's kinetic law:

$$\log \frac{N}{N_o} = -k_{10}\ t$$

In this equation

$$k_{10} = \frac{k}{2.3} = -0.075\ \text{day}^{-1}.$$

In other words, under the conditions of the experiment, the time required to produce 50% mortality is of the order of 4 days in the absence of any bacteriocide.

In the presence of sodium chlorite a clear increase in the mortality appears at concentrations above 0.2 g $ClO_2^-.m^{-3}$. This degree of mortality no longer corresponds to Chick's law. To interpret it, we subtracted the mortality in the absence of chlorite from that observed in its presence. Moreover, we based ourselves on the theory of multiple site inactivation, in which it is considered that a certain number of sites must be reached at least once if the organism is to be completely deactivated. Since the kinetics are first-order for each site considered, the probability of deactivation of m sites is as follows:

$$Pm=(1 - e^{-kt})^m \simeq \frac{N_o - N}{N_o} \quad \text{(fraction of organisms killed)}$$

Thus $$\frac{N}{N_o} = 1 - Pm = 1 - (1 - e^{-kt})^m$$

Binomial expansion gives:

$$Pm = (1 - e^{-kt})^m \simeq 1 - m\, e^{-kt} + \frac{m\,(m - 1)}{2}\, e^{-(kt)^2} \dots$$
$$= 1 - m\, e^{-kt}$$

Thus, the fraction of surviving organisms is:

$$1 - Pm = \frac{N}{N_o} \simeq m\, e^{-kt}$$

and $$\log_{10} \frac{N}{N_o} \simeq \log m - 0.43\, kt$$

According to this, the number of sites m would be about 12. This fairly high number may partially be the result of agglomerations of bacteria, and partially that of the need to reach several vital centres per organism.

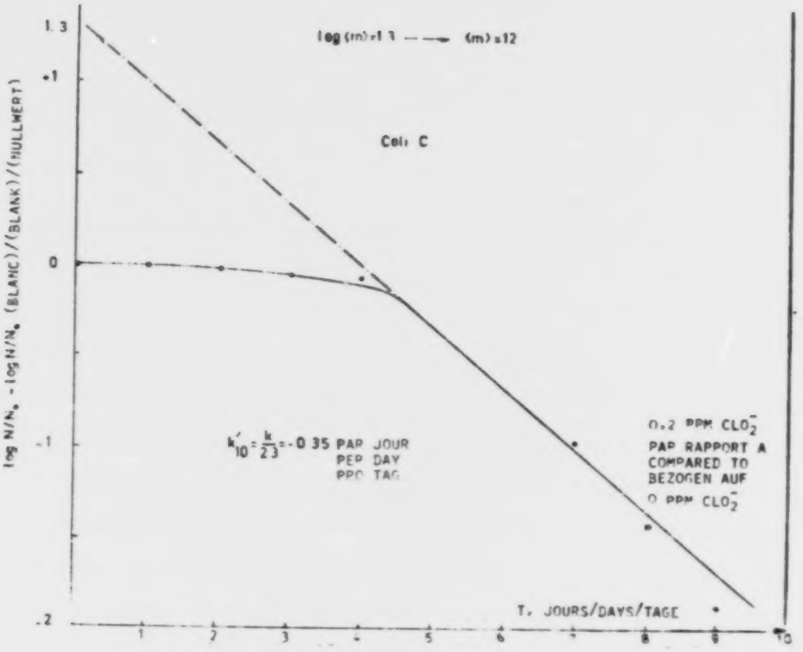


Fig. 4 Action of chlorite on coli C

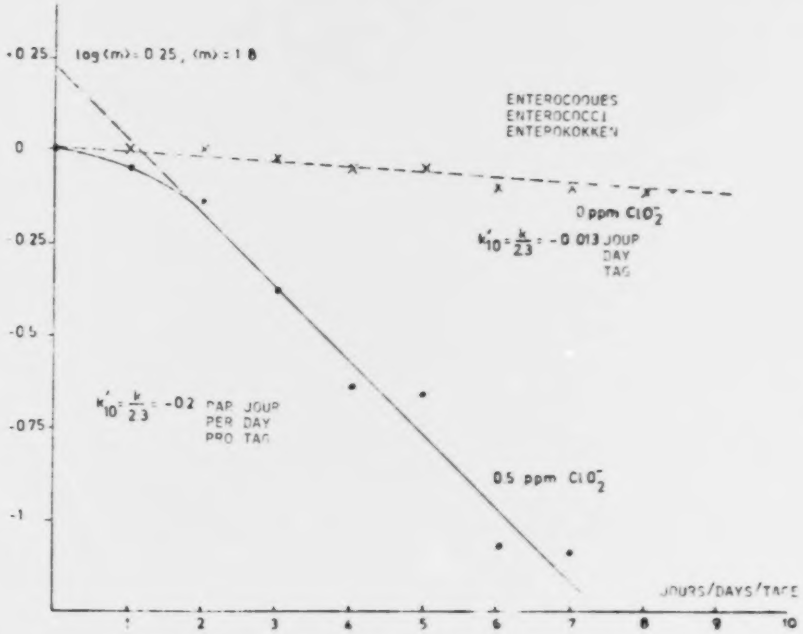


Fig. 5 Action of chlorite on enterococci

As far as enterococci are concerned (a wild strain isolated from the water), a similar argument gives m = 1.8, or about 2. These may have been diplococci.

5.6. Among the ubiquitous microorganisms, Pseudomonas strains deserve special attention since they show a capacity for rapid regeneration in treated waters.

Of the pure strains, Pseudomonas cruciviae has no capacity for surviving longer than a few hours in water. The wild strains that we were able to obtain in cultures seemed generally sensitive to chlorite. In contrast, Pseudomonas putida is more resistant. According to an analysis similar to the preceding one, the mean number of "sites" was about 6, while the concentration factor was of the order of 0.3.

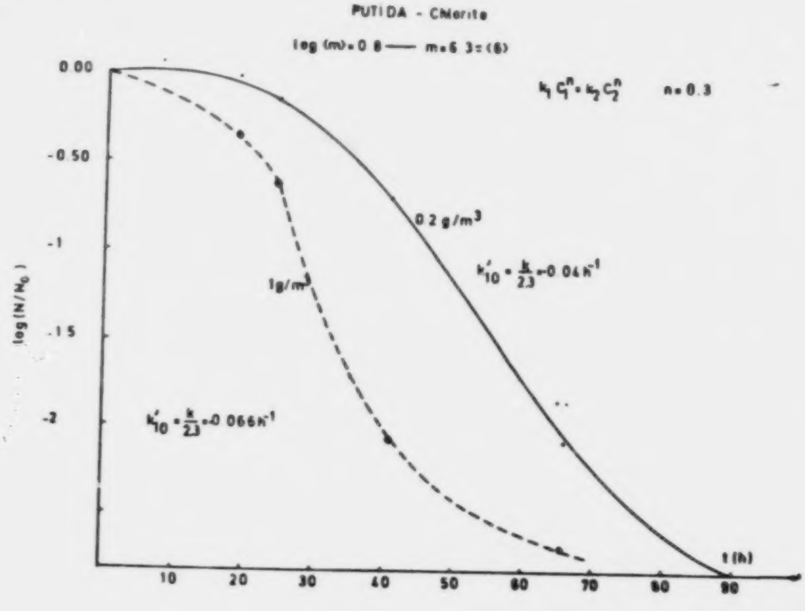


Fig. 6 Action of chlorite on Pseudomonas putida

5.7. Certain cultures were found to constitute exceptions to the rule. Among these, we isolated, on a King F medium, a Rodotorula, which is a ubiquitous non-pathogenic species that can be found among the organisms colonizing the human body. Whereas in water untreated with chlorite the bacterial count decreases progressively as a function of time, it seems that in the presence of chlorite, after a first phase of decline, the microorganism can adapt and maintain an increased level of vitality (Fig. 7). This observation is reported at face value, but it still requires detailed checking before any conclusions can be drawn.

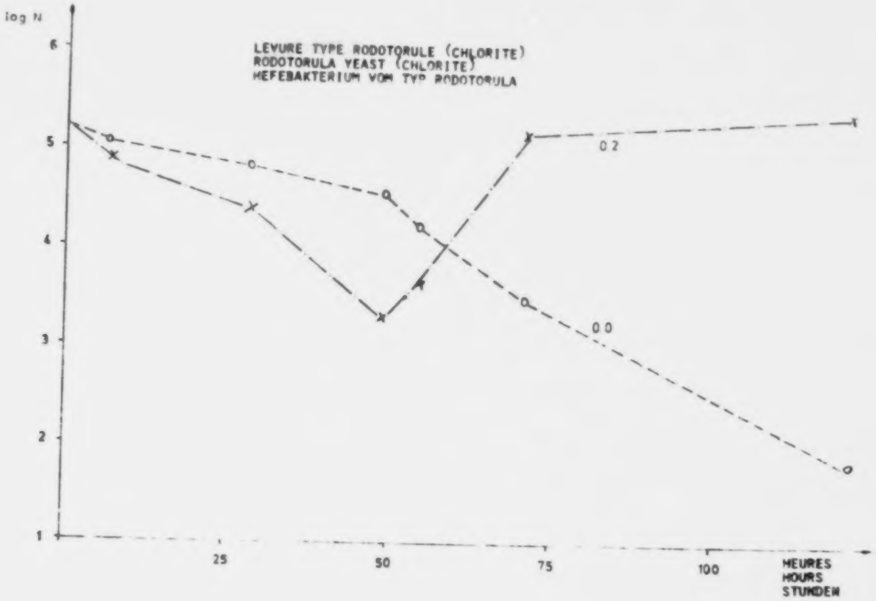


Fig. 7 Action of chlorite on Rodotorula

6. CONCLUSIONS

Though chlorine dioxide has already been in use for several decades for the treatment of drinking water, it often remains an ill-understood reagent. The problems posed by the formation of organochlorine derivatives by chlorination have resulted in a renewed interest in the use of ClO_2. This reagent has great potential: chlorination reduced or eliminated, ability to oxidize organic compounds, higher bactericidal activity in alkaline media compared with chlorine (this activity is maintained in the presence of dissolved ammonia without the need to overchlorinate beyond the critical point), etc.

In the present paper I have reported specific data concerning the use of chlorine dioxide, especially in relation to areas of difficulty:

- Dangers of preparation and handling.
- Toxicity and effects of residual concentrations.
- Analytical methods for the specific determination of chlorine dioxide and residual chlorite.
- Bactericidal and bacteriostatic effects of the dioxide used for post-treatment.

It seems that the objections often formulated against chlorine dioxide do not constitute valid sanitary grounds for opposing its use.

(1) MASSCHELEIN, W.
Les oxydes de chlore et le chlorite de sodium
Ed. Dunod (1969)

(2) MASSCHELEIN, W.J.
Chlorine Dioxide (Chemistry and Environmental Impact of Oxychlorine Compounds)
Ed. Ann Arbor Science (in press)

(3) MASSCHELEIN. W.
Ind. Eng. Chem. Prod. Res. Develop. 6 (1967), 137

(4) APHA-AWWA
Standard Methods (1975)

(5) HODGEN, H.W., INGOLS, R.S.
Analytical Chemistry 26 (1954), 1224

(6) MASSCHELEIN, W.
Analytical Chemistry 38 (1966), 1839

(7) MASSCHELEIN, W.J., FRANSOLET, G.
J. AWWA 69 (1977), 461

(8) KNECHTEL, J.R., JANZEN, E.G., DAVIS, E.R.
Analytical Chemistry 50 (1978), 202

(9) HARTLEY, A.M., ADAMS, A.C.
J. Electroanal. Chem., 6 (1963), 460

(10) MASSCHELEIN, W.J., DENIS, M., LEDENT, R.
(in preparation)

(11) MASSCHELEIN, W.J. FRANSOLET, G.
(in preparation)

(12) U.S. National Board of Fire Underwriters,
Report No. 7 (1949)

(13) HALLER, J.F., NORTHGRAVES, W.W.
Tappi 38 (1955), 38

(14) FRIDLYAND, S.A., KAGAN, G.Z.
Gig. Sanit. 36 (1971), 18

(15) BOGNOLESI, U.
Igiene Mod. 46 (1953), 197

(16) GOMELLA, C.
Techn. Sci. Munic. 56 (1961), 171

(17) DOROLING, L.T.
Water Treatm. Exam. 23 (1974), 190

(18) VILAGINES, R., MONTIEL, A., DERREUMAUX A., LAMBERT, M.
96th Annual AWWA Conference Anaheim (1977)

(19) BANDI, E.E.
Mitt. Geb. Lebensmittelunters. Hyg. 58 (1967), 170

(20) MASSCHELEIN, W., GOOSSENS, R., MINON, M.
Tijdschrift BECEWA (in press)

(21) ASTON, R.N., VINCENT, G.P.
Proc. 9th Ann. Course Water Plant Operators
10 (1947), 54

PRACTICAL EXPERIENCE WITH CHLORINE DIOXIDE AND FORMATION OF BY-PRODUCTS

T. Hedberg, B. Josefsson, C. Roos, B. Lindgren and T. Nemeth

1. Introduction

The use of chlorine dioxide in water treatment plants has increased during the past years. In an EPA-report (1) its extensive use in such countries as West Germany, Switzerland and France are mentioned. Its use in Sweden is also becoming increasingly common. Chlorine dioxide was introduced in 1968 at the water treatment plants in Gothenburg (70 million m^3 per year). In Sweden today about 15% of the supplied water is treated with chlorine dioxide. The reason for its use is, as in most countries, to improve taste and odour, and at the same time increase the disinfection capacity in the distribution system.

Although chlorine dioxide has been used during the last ten years in Sweden, research within this field has only recently started. The general aim is to investigate the oxidation efficiency, by-products and usefulness of different oxidants for the typical surface waters in Sweden. The Swedish waters contain in contrast to most continental waters high concentrations of humic substances and thus they are interesting from a treatment point of view. In addition the waters are - especially in the western and northern parts of Sweden - very soft with a low content of salts and are also rather acidic as a result of long distance transport of air pollution. Since soft waters with a low buffer capacity are very aggressive to pipes, it is common to adjust the pH value to 8-8.5 before distribution.

In addition to the use of chlorine dioxide in water treatment it is also employed in the industry for pulp bleaching. This is in some aspects a related process since in both cases lignin-type compounds are affected. Thus an account of this process is also presented.

2. Formation and behaviour of volatile halogenated organic compounds by chlorine dioxide - chlorine treatment of water in Gothenburg water treatment plant

There has been much concern over the formation of haloforms during the chlorination of water.

In search for safer oxidation techniques attention has been drawn to chlorine dioxide. However, the use of chlorine dioxide may also create undesirable by-products. Chlorine dioxide is a strong oxidant and exhibits a wide spectrum of reactivities towards organic compounds (2). However, to date no chlorinated by-products from the treatment of drinking water with chlorine dioxide have been reported.

Studies of chlorine dioxide bleaching of pulp (section 3) and laboratory experiments on organic model substances provide evidence for production of considerable amounts of organic by-products. On the other hand ,the concentration of reaction products arising from the use of chlorine dioxide in drinking water seems to be comparatively low. Since no volatile organic compounds have been identified as by-products, one must assume that these by-products are dominantly non-volatile. This demands new techniques for analyzing non-volatile compounds in low concentrations.

Presented below are results from analyses of volatile halogenated compounds at different stages in a water treatment plant in Gothenburg, Sweden, that utilizes combined chlorine-chlorine dioxide treatment. The occurrence of these by-products in the distribution net has also been investigated.

The analyses of volatile organohalogens in the drinking water were carried out with two different methods during a two-week period a: closed-loop stripping after Grob (3) followed by $(GC)^2$-MS and b: pentane extraction followed by glass capillary column separation and electron capture detection, $(GC)^2$-ECD (4). The results are presented in Table 2-I. This work has been reported elsewhere (5) in detail.

TABLE 2-I Concentration of organic compounds in drinking water. (The compounds marked with an asterisk were enriched by pentane extraction.)

Halogenated hydrocarbons	Drinking water, ng/l
Dichloromethane^x	< 60
Trichloromethane^x	9500
1,1,1-trichloroethane^x	60
Tetrachloromethane^x	17
Trichloroethene^x	15
Bromodichloromethane^x	2200
Dibromochloromethane^x	600
Tetrachloroethene^x	8
Dichloroiodomethane^x	7
Tribromomethane^x	16
Trichloroaniline	1
Bromonaphthalene	26

Twelve halogenated organic compounds were found of which some were originally present in the raw water, e.g. trichloroaniline.

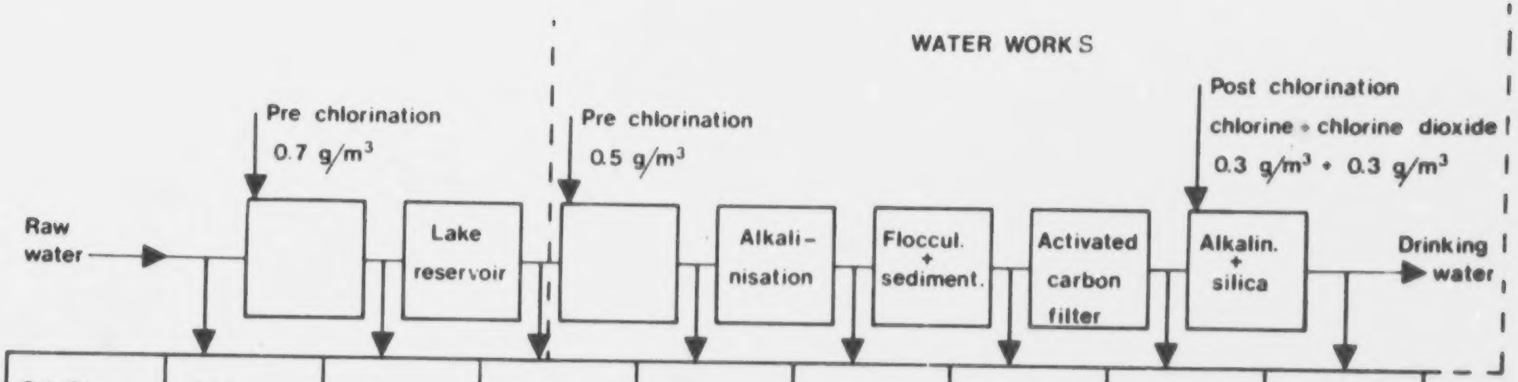
Fig. 2-1 shows the flow scheme of the plant and the concentrations of halogenated compounds. Notable are the markedly increased concentrations of carbon tetrachloride after the different chlorination points. However, this increase is not observed in the prechlorination step of raw water with a high concentration of suspended solids. There seems to be an influence from sedimentation of particulate matter. The increased concentration of carbon tetrachloride probably originates from the added chlorine gas which normally contains 25-100 mg carbon tetrachloride/kg. The reaction of hypochlorous acid with chloroform by an electrophilic attack to yield carbon tetrachloride seems to be insignificant because of the slow reaction rate (6).

Seasonal variations in water quality, e.g. fulvic acid concentration, will affect haloform formation. Samples taken during the winter (Fig. 2-1) show lower contents of haloforms compared with samples taken during the spring (Fig. 2-2).

Concentrations of haloforms in the distribution net over a distance of 30 km in the Gothenburg region (population 600 000) are illustrated in Fig. 2-2. Preliminary evaluation of the results shows an increase of the haloforms with distance from the plants. This might be explained by the generally increasing pH value with distance. The change in pH value is of course dependent on the pipe materials used (concrete-and cement-lined pipes).

Formation of haloforms from chlorine, chlorine dioxide and different combinations of these

Haloforms are produced during chlorination of drinking water. It has been demonstrated that they are formed from degradation products of humic substances (7) which are present in all natural waters.



CH Cl_3	0.14	3.5	1.1	8.9	8.3	4.5	4.5	7.7
$CHBrCl_2$	n.d.	0.5	0.1	2.1	0.6	0.6	0.7	2.0
$CHBr_2Cl$	n.d.	0.013	0.003	0.23	0.04	0.06	0.06	0.50
$CHBr_3$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.009
CCl_4	0.006	0.004	0.004	0.116	0.090	0.050	0.024	0.108
$CHClCCl_2$	0.036	0.027	0.027	0.018	0.018	0.018	0.027	0.108
C_2Cl_4	0.012	0.090	0.090	0.060	0.090	0.012	0.006	0.003

Fig. 2-1 Halogenated compounds in the Lackarebäck Treatment Plant

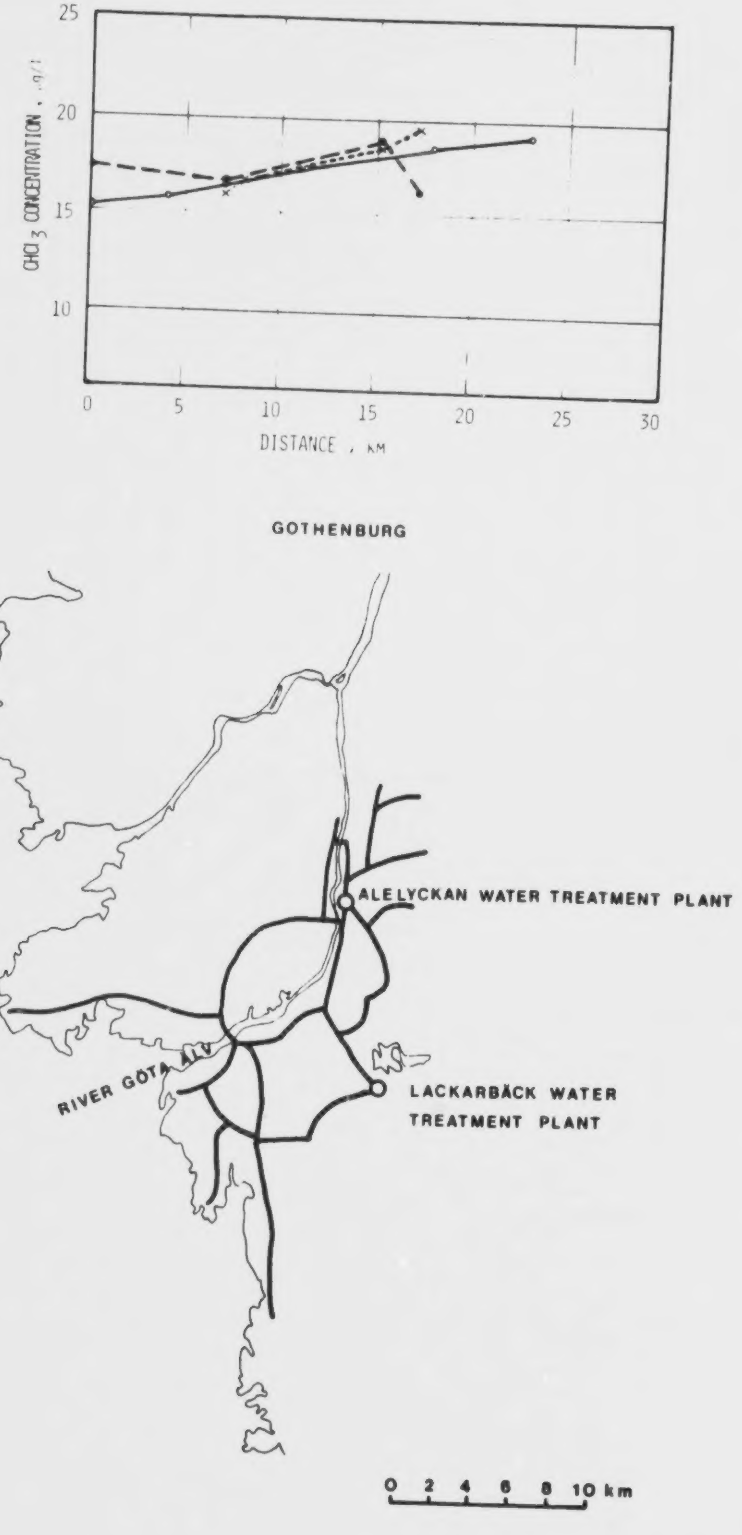


Fig. 2-2 Concentration of trichloromethane in the distribution net

In a series of experiments on a laboratory scale, the formation of haloforms has been studied. River water (pH 6.88), which is the raw water for the water-works in Gothenburg, was treated with chlorine, chlorine dioxide and different combinations of these. Analyses of haloforms were performed by pentane extraction followed by gas chromatography - electron capture detection (4). All experiments were carried out at room temperature. The time-dependence of the haloform formation is shown in Fig. 2-3. Chlorine was added to river water until a concentration of 1 mg/l was reached. The haloforms were analyzed after different periods. The reaction is completed after about 1 hour.

Fig. 2-4 shows the results obtained when river water is treated with different amounts of chlorine. Reaction time 1 hour. At approximately 2 mg/l a plateau level is reached and no additional haloforms are produced when higher amounts of chlorine are added.

Treating river water with chlorine dioxide results in only minor formation of haloforms. This is, however, a result of the small amount of chlorine present in the chlorine dioxide solution used.

Thus chlorine does and chlorine dioxide does not produce haloforms. To investigate the effect of a combination of these, two experiments were carried out. Firstly, chlorine was added to river water at a concentration of 1 mg/l. After 1 hour different amounts of chlorine dioxide were added to the samples. After another hour the samples were analyzed for their contents of haloforms. Secondly, different amounts of chlorine dioxide were added to river water. After 1 hour chlorine was added to a concentration of 1 mg/l. After an additional hour the samples were analyzed for their contents of haloforms. In these experiments pH was kept constant at 6.97 ± 0.07 by a phosphate buffer. The results are

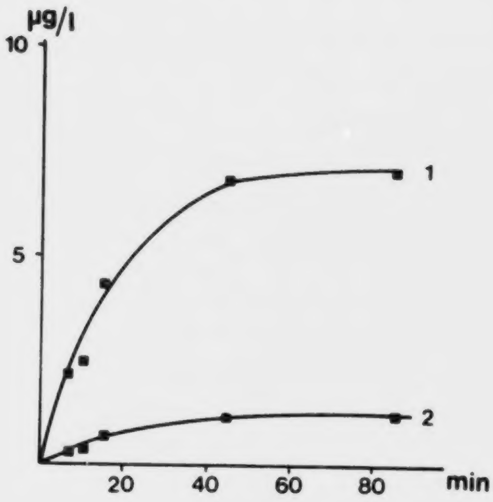


Fig. 2-3

The time dependence of the haloform formation

1 = $CHCl_3$

2 = $CHBrCl_2$

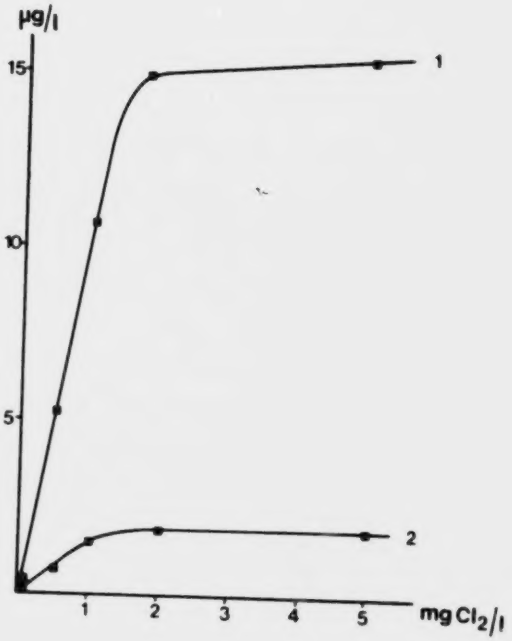


Fig. 2-4

Formation of haloforms from different amounts of chlorine

1 = $CHCl_3$

2 = $CHBrCl_2$

shown in Fig. 2-5. Smaller amounts of haloforms are formed when chlorine dioxide is added before chlorine. It is clear that the adding sequence of chlorine and chlorine dioxide is important with respect to haloform formation. One might assume that chlorine dioxide degrades those compounds which yield haloforms upon chlorination.

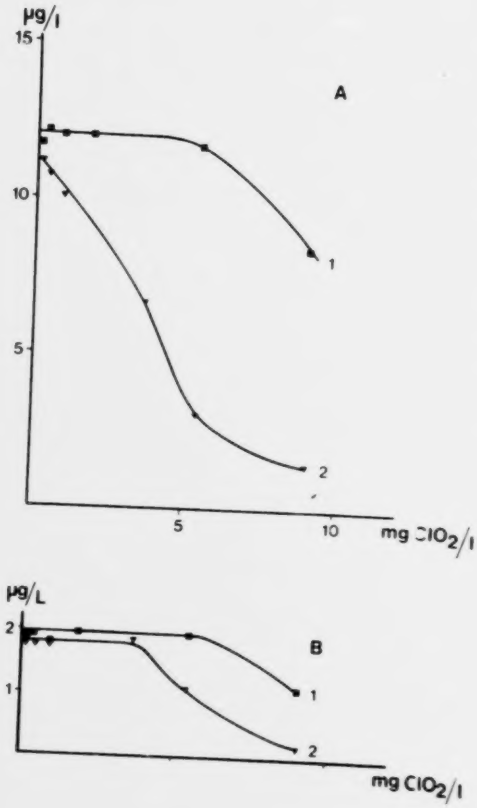


Fig. 2-5

Formation of haloforms from combinations of chlorine and chlorine dioxide
A = $CHCl$; B = $CHBrCl_2$
1 = Chlorine added before chlorine dioxide
2 = Chlorine dioxide added before chlorine

3. Chlorine dioxide in wood pulping industry

Chlorine dioxide is used in wood pulping industry to degrade and dissolve lignin residues in the sulfate and sulfite pulps ("bleaching"). Until now its use has been due mainly to pulp quality demand. In the future, however, the necessity of minimizing the discharge of chlorinated products into lakes and streams will probably result in the increased use of chlorine dioxide as well as oxygen in bleaching in place of chlorine and hypochlorite.

The use of chlorine dioxide in pulp bleaching is very different from its use in water purification. The conditions are for example quite different as shown in Table 3-I. It has, however, one important similarity. The lignin in pulp is a similar material to the humics present in many waters. Both are polymeric aromatic materials.

TABLE 3-I Comparison between conditions during chlorine dioxide bleaching and during water purification with chlorine dioxide.

	Pulp bleaching	Water purification
pH	Start 6, finish 3	6-8.5
Temp.	60-90°C	0-20°C
Time	30-180 min	extensive
Conc. of added ClO_2	5 m mole/l or higher	<0.03 m mole/l

The most reactive positions in lignin and maybe also in humics are the phenolic groups. The lignin phenolic groups are oxidized to quinonic groups and muconic acid groups (Fig. 3-1). Chlorine dioxide is reduced partly to chlorite (1-electron-reduction) and partly to hypochlorite (3-electron-reduction). The hypochlorite formed then reacts either with chlorite (see below) or with lignin.

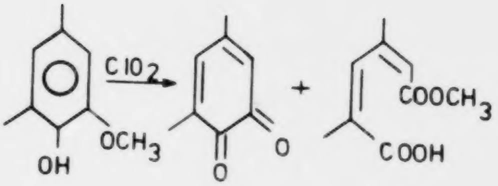


Fig. 3-1

The reaction of phenolic groups of lignin with chlorine dioxide

The concentrations of inorganic chlorine compounds change during bleaching as shown in Fig. 3-2. At first, chlorine dioxide as well as chlorine, which is a companion of chlorine dioxide in all technical chlorine dioxide preparations, are rapidly consumed. The concentration of chlorite increases as long as chlorine dioxide is present but then decreases slowly. Thus chlorite is actually the dominant bleaching agent. As shown in the figure, chlorate is also formed. Its formation is a useless by-product of the bleaching process since it cannot react with lignin. It is also possible that in water treatment the reaction of humics with chlorine dioxide will follow the same pattern described by Fig 3-2.

The reaction between lignin and chlorite involves the transformation of chlorite into chlorine dioxide which then reacts with lignin. The hypochlorite formed by this reaction (see above) oxidizes chlorite into further amounts of chlorine dioxide, which in their turn react with lignin. The process is then a chain reaction.

Whether the reaction of chlorite in water with, for example, humics is a similar chain reaction is difficult to say. The low reactant concentrations are not beneficial for a chain reaction. Chlorite may in water treatment be slowly transformed into chlorine dioxide by an oxido-reduction. If the reaction in the water is a chain process, however, its rate could vary widely depending on the nature of the organic material present.

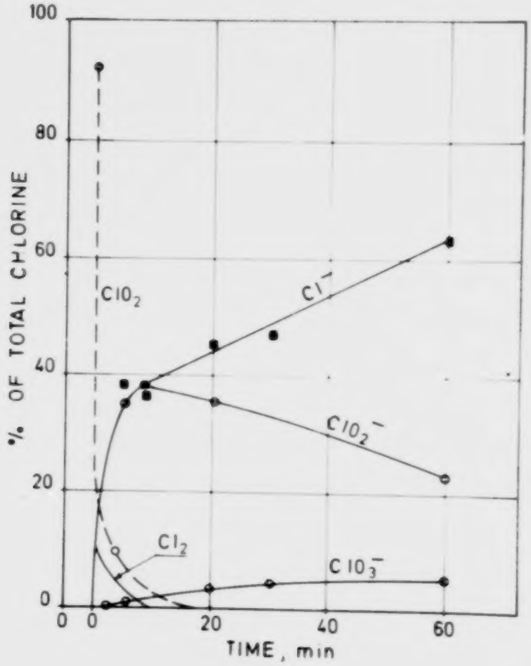


Fig. 3-2 The concentrations of inorganic chlorine compounds during chlorine dioxide bleaching of a sulphate pulp

Oxidation of phenols of different types to those present in lignin yields quinones, quinols and epoxides (Fig. 3-3). The epoxides observed are rather unstable and are not detectable for some hours in water.

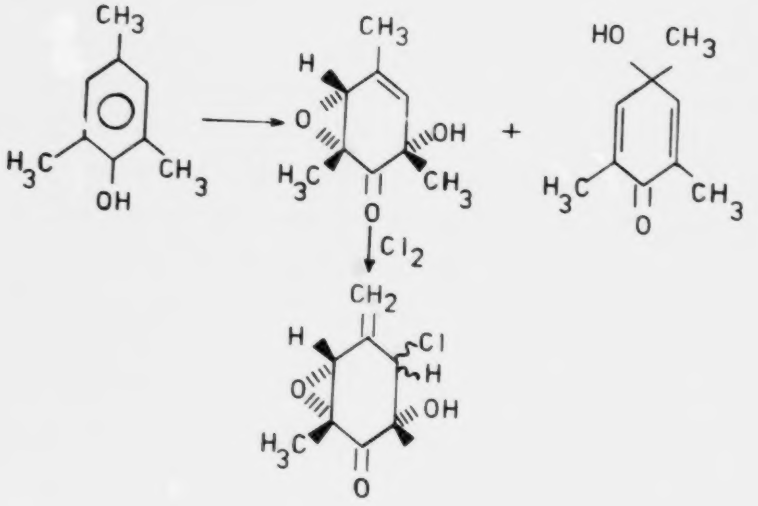
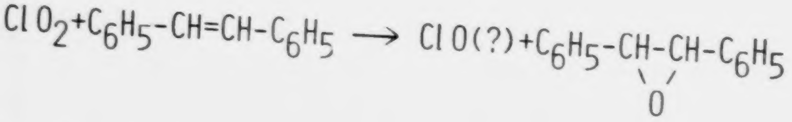


Fig. 3-3 The reaction of mesitol with chlorine dioxide

Chlorine dioxide reacts rather rapidly with double bonds activated by conjugation with benzene nucleus. For example, stilbene is oxidized to stilbene epoxide (Fig. 3-4). The double bond of other stilbenes examined are split by chlorine dioxide.



$$\mathrm{ClO_2 + C_6H_5{-}CH{=}CH{-}C_6H_5 \longrightarrow ClO(?) + C_6H_5{-}\underset{\diagdown\ \diagup \atop O}{CH{-}CH}{-}C_6H_5}$$

Fig. 3-4 One of the reactions of stilbene with chlorine dioxide

An inactivated double bond such as that present in methyl oleate and cyclohexene reacts slowly with chlorine dioxide. Oxidation involves formation of α-chloro-ketones, carboxylic acids and traces of epoxides. The chlorination products of the olefine (di-chloro compounds and chlorohydrins) are formed also by reaction with chlorine dioxide.

Mixtures of chlorine and chlorine dioxide are often used in pulp bleaching. The ratio between the two bleaching agents is then kept at a level which gives a desired effect. For example, addition of a small amount of chlorine dioxide to chlorine gives a more selective attack on the lignin, which spares the cellulose. Chlorine dioxide works as a radical scavenger hindering the radical attack of chlorine on cellulose but not the non-radical attack on lignin. Thus, it is also possible that in water purification good results can be obtained by using mixtures of chlorine and chlorine dioxide.

4. Chlorine and chlorine dioxide for water supply disinfection and taste and odour control; experiences

Disinfection

Chlorine is by far the most commonly used chemical for water disinfection. Chlorine dioxide is used very often for taste and odour control, but it is seldom used for disinfection, even though it is a powerful disinfectant. In fact in certain situations it may be superior to chlorine. However, more information is still needed concerning its potential use as a substitute to chlorine.

Problems with the analyses for chlorine and chlorine dioxide

There are several methods of analyses for chlorine and chlorine dioxide which are well suited for water-works. In measuring chlorine concentrations one usually determines the total halogen concentration of the water. This so-called total chlorine concentration is regarded to be the sum of the free and combined chlorine consisting of chloramines (mono-, di-, and trichloramine). During analyses interactions with other chlorine compounds as well as with bromine and iodine compounds can occur. The total chlorine concentration can thus be written

$$\begin{aligned}
|Cl_2|_{total} = {} & |Cl_2| + |Cl\,NH_2| + |Cl\text{-compounds}| + \\
& + |Cl_2NH| + \\
& + |Cl_3\,N| + \\
& + |Br_2| + |BrNH_2| + |Br\text{-compounds}| + \\
& + |Br_2NH| + \\
& + |Br_3N| + \\
& + |I_2| + |I\text{-compounds}|
\end{aligned}$$

Usually the bromine and iodine compounds can be neglected.

In reality chlorine in water is in equilibrium with hypochlorous acid. At pH values exceeding 5, which is the case in all water treatment processes, the real chlorine concentration is zero. At a pH of 7.4 about 80% of the total chlorine is in the form of hypochlorous acid (HClO) i.e. hypochlorite ion (ClO^-).

This can be seen from the equilibrium curve, Fig. 4-1.

It is well known that the hypochlorite ion has a very low disinfection effect.

Because of the differences in disinfecting power of each species it is desirable to distinguish them. In practice, however, the "chlorine residual" is often measured by the o-toludin method or similar methods which do not distinguish between the different species. Recently a method which makes it possible to distinguish between chlorine and chlorine dioxide has been developed in Sweden (8).

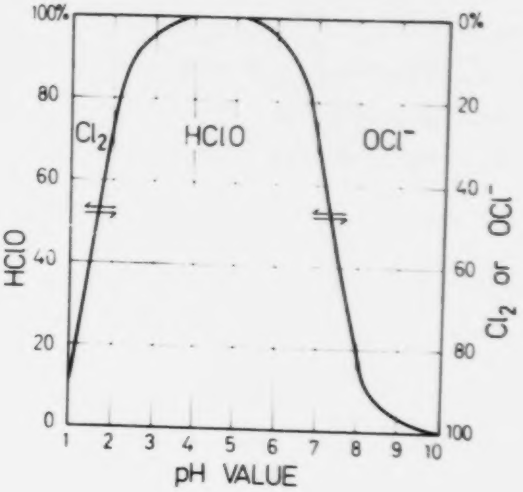


Fig. 4-1

Distribution of chlorine hypochlorous acid and hypochlorite ion in water at different pH values

Behaviour of chlorine and chlorine dioxide as disinfecdisinfectants

In order to prevent precipitation of calcium carbonate in hard waters or to prevent corrosion in soft waters, it is necessary to bring about equilibrium in the calcium carbonate - carbonic acid system prior to the distribution. In a very soft water, which is common in Sweden this equilibrium cannot be obtained with the usual techniques. It is actually necessary to increase the water hardness which is an expensive process. In order to protect the pipes, and especially the copper pipes, the pH value is normally kept as high as 8.5. At this pH value the disinfection capacity of the water is decreased, which may lead to unsatisfactory quality in case of a secondary contamination.

The measurements of combined chlorine may not be satisfactory for control of disinfection. Chloramines are frequently used for disinfection in the distribution system. It has been shown (9) that the various combined chlorine compounds may be different from one another in capacity to inactivate bacteria or virus.

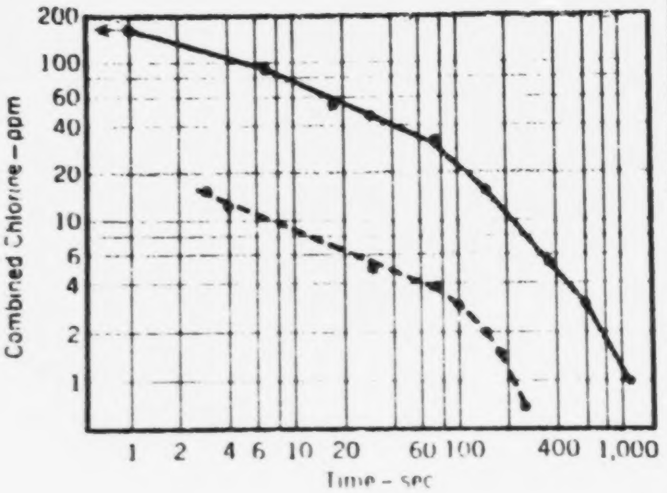


Fig. 4-2 Chlorination of Esch coli (37°C, pH 7), using different forms of combined chlorine (9)

The equivalents of combined chlorine are plotted against the time for a one log reduction of the concentration of live bacteria. The solid curve indicates results obtained by the use of chloramine T; the dashed curve shows results obtained by the use of NH_2Cl.

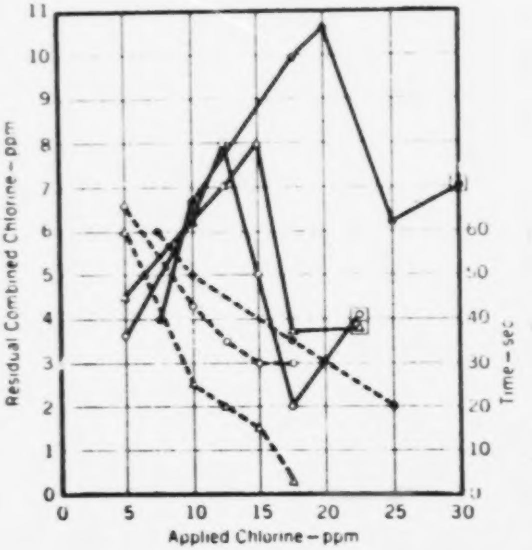


Fig. 4-3 Free residual chlorination

The solid curves indicate the relationship between the applied concentration of free chlorine added to a constant concentration of ammonia and the residuals found of combined chlorine. The squares indicate the first values at which residuals of free chlorine were also demonstrable. The dotted curves represent the rate of reduction of live Esch coli at 37°C and pH 7. The time in seconds for a one log unit reduction is plotted against the applied concentration of chlorine. Identical symbols are used for corresponding curves for each of the three experiments.

Most experiments with bacteria have been made either with Escherichia coli or with bacteria described as belonging to the coliform group. However, Ridenour and Armbruster (10) carried out extensive experiments with different bacteria. For all the organisms they observed similar results for chlorine or chlorine dioxide. They concluded that E. coli was more resistant to chlorine or chlorine dioxide than any of the bacteria on their list which could be considered pathogenic.

At neutral pH values, parallel experiments by a number of researchers have shown chlorine and chlorine dioxide, at equal concentrations, to be about equally effective against E. coli (Bernarde, et al, (11), Berndt (12), and Ridenour and Armbruster,(10)). We have obtained similar results in laboratory experiments on coliform group bacteria in Göta Älv raw water (Gothenburg). The effects of variations in pH value were also examined. The effectiveness of chlorine was observed by all investigators to diminish with increasing pH value of the water (eg. Fair and Geyer, (13)).

With chlorine dioxide, however, there has been no such agreement among different investigators. Ridenour and

Armbruster (10) observed that chlorine dioxide was at least as effective at pH 9.5 as at pH 7. The experiments were performed with E. coli added to chlorine demand free water.

Bernarde et al.(11) found that chlorine dioxide was more effective at pH 8.5 than at pH 6.5. A different relationship was observed by Berndt (1965). These experiments were made using raw water from the water-works at the city of Lübeck. The result showed that chlorine as well as chlorine dioxide were more effective at lower pH values (pH 5) than at higher pH values (pH 9.3).

Experiments with bacterial spores have shown that chlorine dioxide is more effective than chlorine when these chemicals were compared at equal concentrations (Ridenour and Armbruster (10), Berndt (12)).

Some comparative studies (Gothenburg 1978) on total counts of bacteria at 22° in drinking waters disinfected by different techniques were performed. The streak plate method was used for growth tests on Nutrient Agar (Oxoid Type CM3), Tryptone Soya Agar (Oxoid Type CM 131) and Fe Pa medium according to Ferrer, et al.(14). The first results show that on all the media used growth is more often obtained from samples taken from the distribution system of Uppsala (chlorine treatment) than from the chlorine-dioxide treated water of Gothenburg.

Considerable data has been published during the past twenty years showing the effectiveness of chlorination against different viruses under different conditions. In general, free chlorine in water effectively inactivated the different viruses which were tested. Furthermore, chloramines or other combined chlorine forms were found to be much less effective.

Chlorine and chlorine dioxide have been compared for effectiveness against poliovirus (Ridenour and Ingols, 1946). At that time it was not possible to titrate a virus concentration so conveniently and accurately as it is today. It appeared that chlorine dioxide added to a virus suspension at pH 7 was more effective than an equivalent dosage of hypochlorite.

The effects of changes in the pH value have also been studied. In the range pH 5 to pH 9 chlorination has been consistently more effective in laboratory testing at the lower pH values.

On the other hand, several investigators have shown that chlorine dioxide inactivates viruses faster at higher pH values than at lower pH values. Cronier et al. (15) showed a three-times faster inactivation of poliovirus 1 at pH 9.0 than at pH 7.0. Warriner (16) showed the same effect on poliovirus 3. This effect was more marked at higher dosages, Fig. 4-4, Table 4-I.

When 0.2 mg Cl_2/l was added together with 0.5 mg ClO_2/l no improvement relative to 0.5 mg ClO_2/l alone was noticed.

Thus chlorine dioxide appears to be a better alternative from a microbiological point of view than chlorine since it is most effective in the pH range in which water is distributed.

Except for the generalizations about the effect of pH noted above, the results of many virus inactivation investigations have been contradictory. The practical application is limited because chlorination according to the same procedure may give different results in different waters (Engelbrecht, et al. (17)). The difficulty is enhanced because it is not practical to make routine virological isolation tests in the manner that routine bacteriological testing can be carried out on

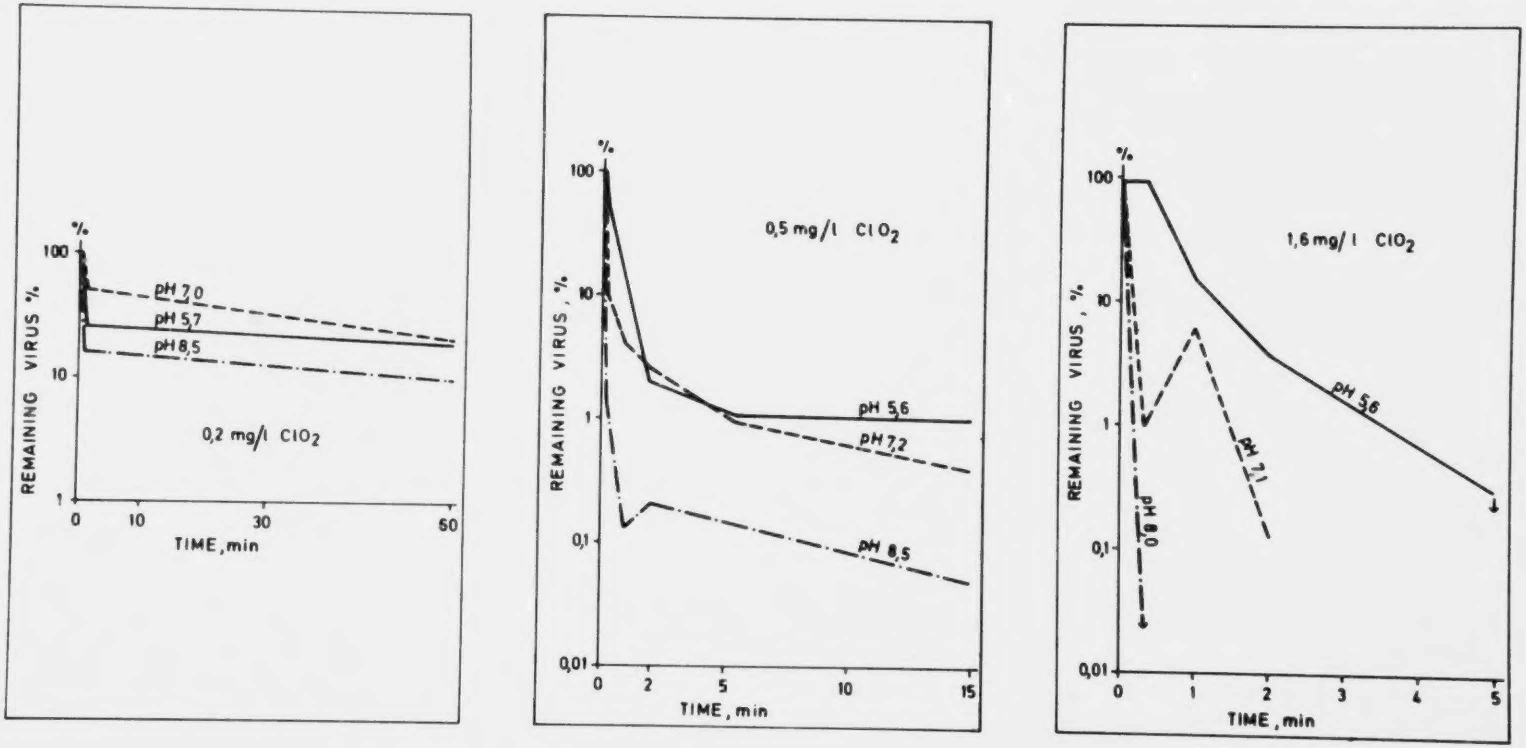


Fig. 4-4 Remaining virus as a function of contact time at different dosages of chlorine dioxide at different pH values (16)

TABLE 4-1 Inactivation of poliovirus with chlorine dioxide at 20 °C. The redox potential is measured against a calomel electrode.

Parameter	Test No. 1			Test No. 2			Test No. 3	
	0.2 mg ClO_2/l			0.5 mg ClO_2/l			1.6 mg ClO_2/l	
	pH 5.7	pH 7.0	pH 8.5	pH 5.6	pH 7.2	pH 8.5	pH 5.6	pH 7.1
Redox potential, mV								
without virus	610	440	360	670	660	580	720	705
with virus	360	330	260	630	580	270	700	690
Amperometric titration of chlorine-chlorine dioxide residual, mg/l								
chlorine	0	0	0	0	-	0	0.02	0.03
chlorine dioxide	0.07	0.03	0.03	0.27	-	0	1.40	1.41
chlorite	0.11	0.11	0.12	0.12	-	0.41	0.07	0.08
Conc. of surviving virus (log ID_{50}/0.1 ml)								
without chlorine dioxide	3.2	3.8	3.8	2.8	2.5	3.5	2.0	2.5
with chlorine dioxide,								
after 10-20 sec	2.4	3.4	3.6	1.8	2.2	1.6	2.0	0.5
after 1 min	2.6	3.5	3.0	1.4	1.6	0.6	1.2	1.3
after 2 min	-	-	-	1.2	0.8	0.8	0.6	-0.4
after 5 min	-	-	-	0.8	0.5	-	<-0.5	-
after 15 min	-	-	-	0.4	0.5	0.2	-	-
after 60 min	2.5	3.2	2.8	0.4	0.5	0.4	-	-

both raw and treated water. However, investigations by Lund (18, 19) have revealed a relationship between oxidation potential and the rate of virus inactivation. This work has opened the possibility of regulating chlorination, including chlorine dioxide treatment, for the purpose of inactivating virus.

Figure 4-5 shows results obtained for the inactivation of poliovirus using chloramines (9). It shows the range of potential measurements (with a calomel reference electrode) which are likely to be of interest in water treatment. Among the practical questions raised concerning this procedure are the difficulties encountered in measuring potentials and the effectiveness in controlling the bacteria.

The oxidation potentials are plotted against the time in minutes needed for a reduction of one log unit of active virus.

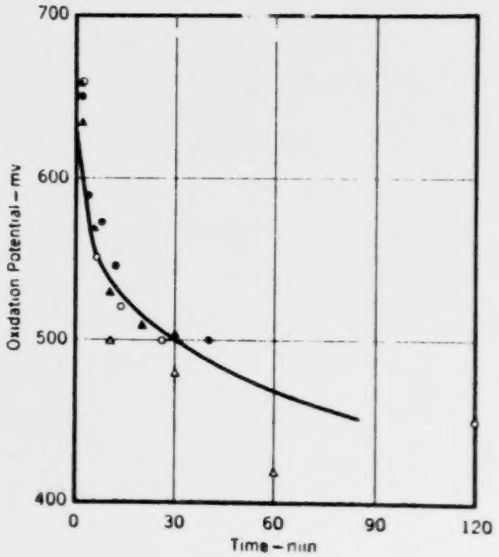


Fig. 4-5

Oxidation potentials obtained by chlorination of poliovirus (37°C, pH 7) (9)

The common denominator for disinfection chemicals is thus their ability to break through the redox buffer capacity and thereafter change the redox potential. The redox potential of a chlorine solution is strongly dependent on the pH value, as can be seen from Fig. 4-6. The redox potential decreases with increasing pH and the possibility to break the redox buffer capacity is thus reduced. In soft waters, in which it is necessary from a corrosion point of view to have a high pH value, a five-times higher chlorine concentration as in hard waters is required and still the disinfection effeciency cannot be guaranteed.

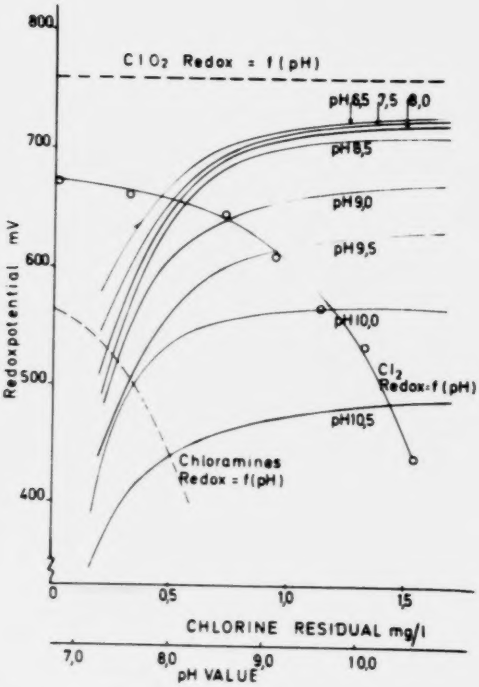


Fig. 4-6 The redox potential as a function of the chlorine residual and as a function of the pH value for chlorine dioxide (---), chlorine (-θ-) and chloramines (- - -)

Transformation of chlorine by ammonia to chloramines results in a radical decrease of the redox potential which in turn lowers the disinfection effect. In other words, to be able to indicate a "chlorine residual" in the distribution system one deliberately decreases the efficiency of the dosage.

Chlorine dioxide has a higher redox potential than chlorine. In addition, the potential is almost independent of changes in the pH value.

5. Experiences with chlorine dioxide for taste and odour control

Undesirable taste and odour in drinking water have been noticed a very long time ago, and they are still a problem especially in industrialized and densely populated areas. Many of the taste-producing or odourous substances are still unknown. The origin of these substances varies. It may be domestic sewage, chemical industries, bacteria, fungi and algae.

Consumers are aware of the deterioration in their environment and refuse to accept drinking water not in excellent condition. Removal of taste and odour is therefore a necessity at many water-works. Several methods exist but often it is impossible to achieve the desired effect with only a single method. Sometimes it is necessary to control the pollution at the raw water source, apply some process in the water treatment and then carefully control the distribution system.

This was the case in Gothenburg. Early investigations (20) of taste and odour control at the water treatment plant including slow sand filtration, treatment with powdered activated carbon, ozone and chlorine dioxide, showed a satisfactory result by using a mixture of chlorine and chlorine dioxide, Fig. 5-1.

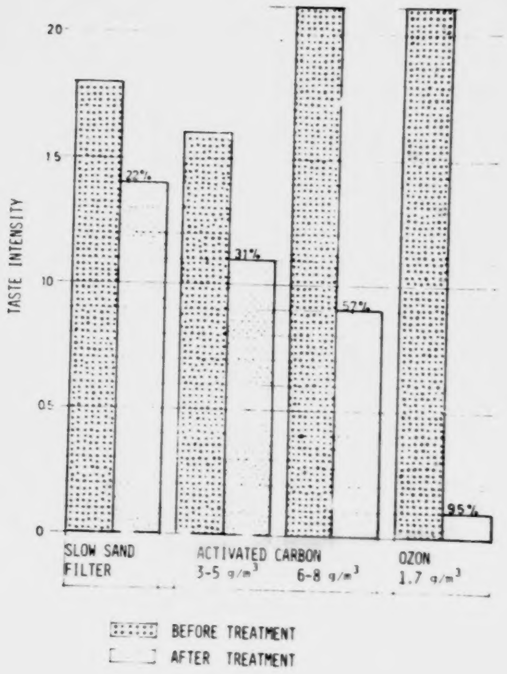


Fig. 5-1

Results from taste control investigations

Subsequently the raw water source - the river Göta Älv - was contaminated by wastes and this, of course, affected the taste and odour. The raw water intake was rebuilt and the river water was pumped to a natural lake acting as a reservoir. Together with increased river pollution control, the situation was markedly improved. An additional problem then arose occasionally - during spring and autumn a mass production of algae in the lake resulted in taste and odour in the water. On such occasions chlorine dioxide treatment alone was insufficient and therefore granular activated carbon was introduced and has been used for nearly 10 years.

In the taste and odour investigations in Gothenburg it was noted in agreement with others(1) that it is possible to have a higher "chlorine residual" with chlorine dioxide than with chlorine, without producing a chlorinous taste (Fig. 5-2).

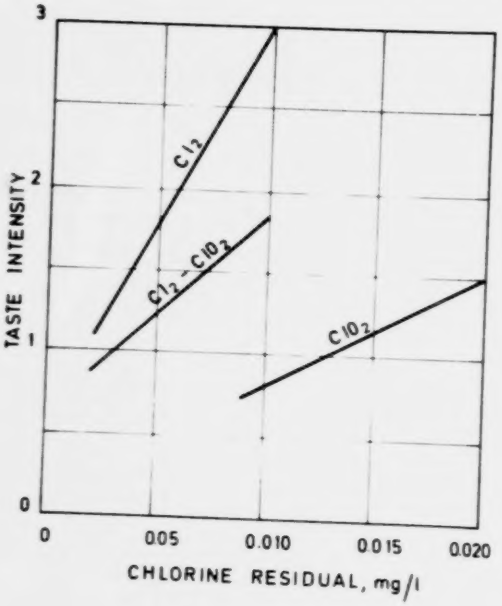


Fig. 5-2

Taste intensity as a function of the "chlorine residual" from the different methods of treatment

We conclude the following: chlorine dioxide can improve the taste and odour and does not form haloforms. Furthermore, chlorine dioxide is an excellent disinfectant in the distribution system and this facilitates the supply of a safe and potable water.

(1) U.S. Environmental Protection Agency
Ozone, Chlorine Dioxide and Chloramines as Alternatives to Chlorine for Disinfection of Drinking Water
State-Of-The-Art, Nov. 1977

(2) GORDON, G., KIEFFER, R.G., ROSENBLATT, D.H.
The Chemistry of Chlorine Dioxide
Progress in Inorganic Chemistry, Wiley-Interscience, New York 15 (1972), 259-286

(3) GROB, K., ZÜRCHER, F.
Stripping of trace organic substances from water, equipment and procedure
J. of Chromatography 112 (1976), 285

(4) EKLUND, G., JOSEFSSON, B., ROOS, C.
Determination of Volatile Halogenated Hydrocarbons in Tap Water, Seawater and Industrial Effluents by Glass Capillary Gas Chromatography and Electron Capture Detection
J. High Res. Chrom. 1 (1978), 34-40

(5) EKLUND, G., JOSEFSSON, B., ROOS, C.
Trace Analysis of Volatile Organic Substances in Göteborg Municipal Drinking Water
Vatten 31 (1978), No. 3

(6) MORRIS, J.C.
The Chemistry of Aqueous Chlorine in Relation to Water Chlorination
Water Chlorination, Environmental Impact and Health Effects
Ann Arbor Science, Ann Arbor 1 (1978), 21-35

(7) ROOK, J.
Chlorination Reactions of Fulvic Acids in Natural Waters
Environ. Sci. Technol. 11 (1977), 5, 478-482

(8) ISACSSON, U., WETTERMARK, G.
Selective analysis of chlorine (hypochlorous acid) and chlorine dioxide using chemiluminescence
Anal. Lett. 11 (1978), 13-25

(9) KJELLANDER, I., LUND, E.
Sensitivity of Esch Coli and Poliovirus to Different Forms of Combined Chlorine
J. AWWA 57 (1965), 893

(10) RIDENOUR, G.M., ARMBRUSTER, E.H.
Bactericidal Effect of Chlorine Dioxide
J. AWWA 41 (1949), 537

(11) BERNARDE, M.A., ISRAEL, B.M., OLIVIERI, V.P., GRANSTRÖM, M.L.
Efficiency of Chlorine Dioxide as a Bactericide
Applied Microbiology 13 (1965), 776

(12) BERNDT, H.
Untersuchungen zur Wasseraufbereitung und Wasserdesinfektion mit Chloridoxyd, insbesondere zu Fragen der pH-Wert-Abhängigkeit und der Chloritrückbildung
Arch. Hyg. 145 (1965), 10

(13) FAIR, G.M., GEYER, J.C., OKUN, D.A.
Water and Wastewater Engineering, Wiley 2 (1968), 31-18

(14) FERRER, E.B., STAPERT, E.M., SOKOLSKI, W.T.
A Medium for Improved Recovery of Bacteria from Water
Can. J. Microbiol. 9 (1963), 420-422

(15) CRONIER, S., SCARPINO, P.V., ZINK, M.L., HOFF, J.C.
Destruction by Chlorine Dioxide of Viruses and Bacteria in Water
Abstr. Ann. Meeting American Soc. for Microbiol. (1977)

(16) WARRINER, R.
Inactivation of Poliovirus with Chlorine Dioxide
Vatten, Arg 23 (1967), 284-290

(17) ENGELBRECHT, R.S., WEBER, M.J., SCHMIDT, C.A., SALTER, B.L.
Virus Sensitivity to Chlorine Disinfection of Water Samples
EPA-600/2-78-123

(18) LUND, E.
Inactivation of Poliomyelitis Virus by Chlorination at Different Oxidation Potentials
Arch. Ges. Virusforsch. 11 (1961), 330

(19) LUND, E.
Effect of pH on the Oxidative Inactivation of Poliovirus
Arch. Ges. Virusforsch. 12 (1963, 1

(20) Investigation of Different Methods for Taste and Odour Improvement
Chalmers Univ. of Tech., Dept. of Water Supply and Sewerage, Series B 64 (1964), 1

REMOVAL OF ORGANIC MATTER FROM WATER BY UV AND HYDROGEN PEROXIDE

L. Berglind, E. Gjessing and E. Skipperud Johansen

1. Introduction

In 1966 Armstrong and coworkers (1) introduced a method for the removal of organic matter from samples of water to be analyzed on total phorphorus. Samples of alcohols, carbohydrates, organic acids and humic acid in aqueous solutions were exposed to ultraviolet (UV) irradiation in the presence of oxygen. It was found that the content of organic compounds was reduced below detectable levels. The only final product which was registered was carbon dioxide, CO_2.

It has been noticed that sunlight may induce both fading of the colour and reduction of organic matter in water (2,3).

Elimination of organic pesticides has also been carried out by photo-induced oxidation (4,5) as well as photo-induced decomposition of formic acid and dodecyl benzene sulfonate in aqueous solutions (6,7). Photo-oxidation of refractory organic compounds in municipal wastewater has been given increased attention during the past years (8,9). The process of oxidation is usually very complex. Some highly reactive intermediates are involved. One of these is the hydroxyl radical $OH^\cdot$, which is formed during light absorption (7,10, 11). The rate of oxidation is primarily limited to the yield of $OH^\cdot$. For the purpose of water purification, the method of photo-oxidation requires an excess of $OH^\cdot$. One way to obtain this is by adding hydrogen peroxide (H_2O_2) to the system. It is known that UV irradiation may induce breakdown of H_2O_2 into hydroxyl radicals and thereby accelerate the process of oxidation (1,11,12).

2. Earlier Results

In the late sixties we suggested that some 20 % of the observed reduction of humus colour in lakes and rivers may partly be due to natural UV radiation and that this principle should be considered as an alternative method for the purification of surface water based on artificial UV (13). Laboratory experiments showed that humus in water, which is persistent soil originating organics, were completely mineralized by a combination of UV radiation and hydrogen peroxide. Several other oxydants were also tested together with the UV, such as O_3, O_2 and air. However, H_2O_2 appears to be outstanding with respect to these effects. Some results are summarized in Table 1.

TABLE 1: Effect of UV radiation of aquatic humus. Per-cent reduction of colour (or increase(+)) and organic carbon by different "doses" of UV radiation under various conditions.

"Chemical" added	Colour Minutes of Radiation 1	 5	 20	 60	Organic Carbon Minutes of Radiation 1	 5	 20	 60
Air	+ 2	+ 6	13	41	6	13	23	41
N_2	+ 1	+ 2	11	16	0	5	11	26
Air (pH 7)	+12	+10	+ 8	25	6	9	16	19
Air (pH 3)	+ 5	4	14	35	0	3	14	15
H_2O_2	45	97	98	99	43	73	92	100
Cont.aeration	6	0	21	-	2	2	10	-
BaO_2 + air	11	8	10	-	9	11	16	-

Essentially the same procedure as that used for humus was also used on an aqueous solution of the polyaromatic hydrocarbon, 3.4-Benzopyrene (B(a)P) : 99 % removal from a 100 µg/l solution resulted.

It is strongly believed that the combination of UV and H_2O_2, being so effective as to mineralize humus (and B(a)P), might be a potential method for the removal of organics from water. However, is it practical and what will it cost? The purpose of the present work is to gather more information around these two questions.

3. Recent Results

In a set-up as illustrated in Figure 1 different kinds of organic matter were recirculated for several hours. Samples were collected periodically. In Table 2 the tested organics and chemicals are listed.

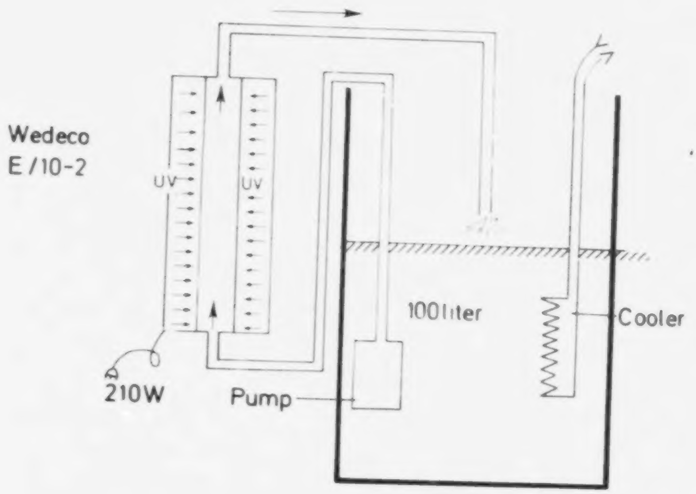


Fig. 1 UV-radiation plant. The radiation unit consists of a quartz tube surrounded by 6x30 W UV lamps (254 nm). The hydrogen peroxide is added to the water in the tank immediately before start. The pumping rate was 0.8 l/sec.

TABLE 2: The water samples and chemicals tested in the UV pilot plant

	Colour mg Pt/l	TOC mg C/l	Cond. µS/cm	pH	Conc. µg/l
1. Humus water	109	14,5	31	4,9	-
2. Humus water	27	4,2	32	6,2	-
3. 3,4-Benzopyrene	-	-	-	-	65
4. 2-Methylisoborneol (MIB)	-	-	-	-	1
5. Chloroform/bromodichloromethan (BDCM)	-	-	-	-	100/100

Humus

Eight 50-litre aliquotes of humus sample No. 1 were circulated for four hours (0.8 l/sec) in the system illustrated in Fig. 1, with different amounts of 35 % H_2O_2 added, ranging between 0 and 50 ml/l. Water samples were collected after 30, 60, 120, 180 and 240 minutes and analyzed on colour and TOC. The relationship between colour- and TOC removal and the amount of H_2O_2 added is illustrated in Fig. 2. 120 minutes radiation is considered.

Humus sample No. 2 showed the same H_2O_2 response with regard to humus removal, namely: maximum effect with 0.2 ml of 35 % H_2O_2 per litre. It is interesting and important to note that higher concentrations of H_2O_2 did not result in a better removal of organic matter and that the amount of H_2O_2 appears to be independent of the amount of humus.

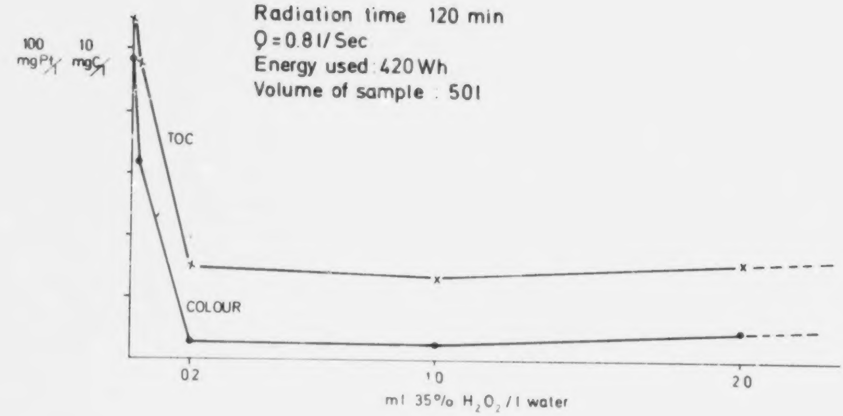


Fig. 2 The relationship between TOC colour removal and the amount of hydrogen peroxide (H_2O_2) added at a fixed "UV dose"

In Figure 3 the "UV dose"-response relationship regarding colour removal with a fixed H_2O_2 dose (0.2 ml 35 % H_2O_2/l is plotted. Fig. 4 shows the corresponding reduction of total organic carbon.

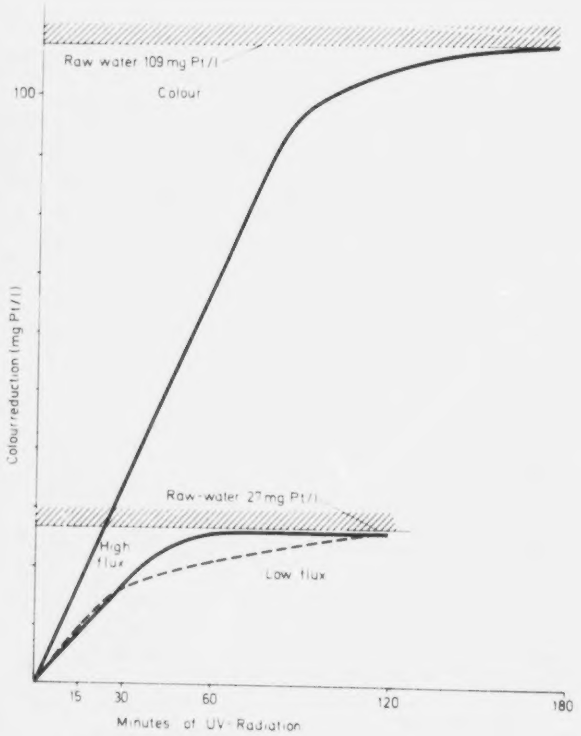


Fig. 3

Reduction of humus colour with different "UV doses"; 0.2 ml 35 % H_2O_2/l added. The low-coloured water is also run with low flux (0.2 l/sec). It was noticed that the colour of the samples collected during the run was reduced during 1-2 days of storage

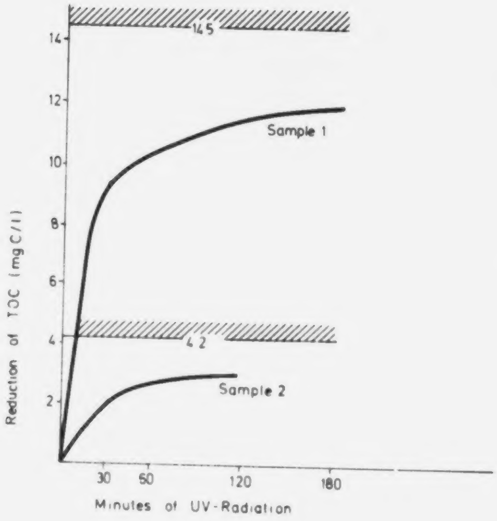


Fig. 4

Reduction of total organic carbon (TOC) in two different humus samples with different "UV doses" and 0.2 ml 35 % H_2O_2/l added. The TOC analyses are to some extent uncertain, probably due to some interfering substances in the samples.

Figure 5 illustrates the percent reduction (with time) of colour and TOC.

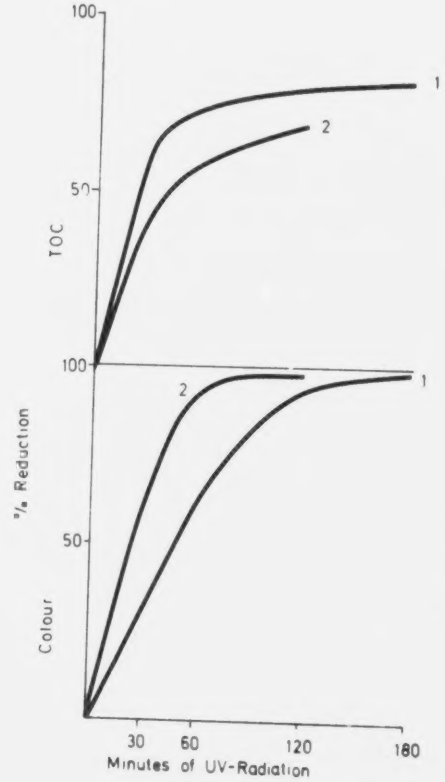


Fig. 5

Percent reduction of colour and organic carbon in two different humus samples with different "UV doses" and with 0.2 ml 35 % H_2O_2/l added.

In the brief discussion below,the carbon results are omitted because at present we are uncertain as to whether the routine method used (wet oxydation in glass ampulla and IR determination of the resulting CO_2) is appropriate for these samples. Considering Figure 3, it appears that the same "UV-dose" (and amount of H_2O_2) removes, in the beginning of the process, twice as much colour from the highly-coloured water (109 mg Pt/l) as from that of low colour (27 mg Pt/l).

The results suggest that the apparent linear colour reduction is levelling off when the residual colour is in the range of 10 mg Pt/l.

Figure 3 shows that there is only need for twice as much energy to reduce the "109-coloured" water by 95 % as that for "27-coloured" water. All this suggests that, under the conditions outlined, the method appears to be relatively most effective on highly coloured waters.

Organic Chemicals in Water

100 litres of distilled water, containing the concentrations and chemicals listed in Table 2, were recirculated for 1 - 4 hours. Samples were taken at different time intervals and analyzed on the chemical substance concerned. The results are given in Table 3.

The results are also illustrated in Fig. 6. In general, these results show more than 90 % reduction of the chemicals treated with UV radiation for 2 hours. MIB, which is one of the chemicals responsible for a characteristic soil smell and -taste, which may appear in drinking water reservoirs, is removed below detectable limits within 30 minutes.

TABLE 3: Removal of organic chemicals from water with UV radiation and hydrogen peroxide

			μg/l				
without H_2O_2				with 0.1 ml 35 % H_2O/l			
Min. UV-Radiation	B(a)P x)	Chloroform	BDCM x)	B(a)P x)	MIB x)	Chloroform	BDCM x)
0	65(0)	100(0)	100(0)		1	100(0)	100(0)
30	-	-	-		0(100)	75(25)	58(42)
60	-	92(8)	91(9)	18(72)		68(32)	44(56)
120	42(29)	42(58)	75(25)	6(91)		9(91)	9(91)
240	-	-	-	1(98)	-	-	-

x)
B(a)P: 3,4-Benzopyrene
MIB: Methylisoborneol
BDCM: Bromodichloromethan
( ): denotes percent-reduction

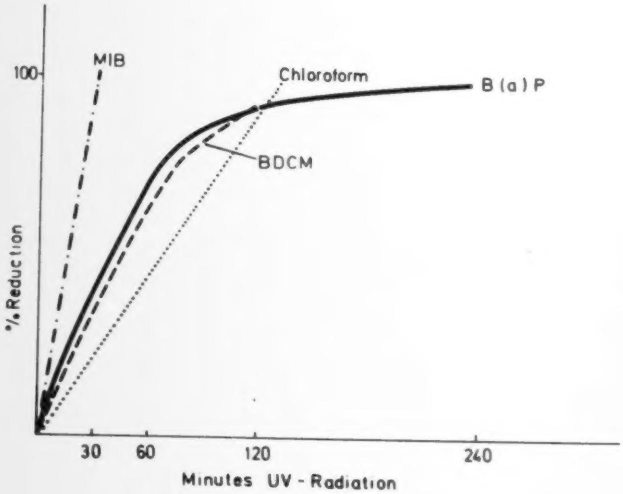


Fig. 6

Percent reduction of chemicals in aqueous solutions with different "UV doses"; 0.1 ml 35 % H_2O_2/l was added.

MIB = Methylisoborneol
BDCM = Bromodichlormethane
B(a)P= 3.4 Benzopyrene

4. Cost Estimates

Except for MIB and the low humus-coloured water, it appears from the results that, with a H_2O_2 dose of 0.1 - 0.2 ml 35 %/l and at 120 minutes of radiation, a 90 - 95 % removal is achieved.

Considering 50 % removal and the following price estimates:

				$
Electric energy		Nkr/kWh	0.15	(0.03)
H_2O_2 (35 %)		Nkr/l	3.85	(0.70)
UV-lamps	Nkr. 2.200.-			
Pilot plant	Nkr. 15.000.-			
Lifetime of UV-lamps 10.000 hours		Nkr/h	0.22	(0.04)
10 % interest of Plant cost		Nkr/h	0.17	(0.03)

In Table 4 the resulting costs are shown.

TABLE 4: Estimated cost of water with 50 % removal of the organic matter. All figures are in Nkr (or $) per m^3.

Sample	H_2O_2	El. Energy	Lamp	Plant	Total Nkr.	$
1 Humus 1	.8	.2	1.5	1.1	3.6	.65
2 Humus 2	.8	.4	2.7	2.1	6.0	1.10
3 B(a)P	.4	.2	1.5	1.1	3.4	.62
4 MIB	.4	.1	.6	0.4	1.5	.27
5 Chloroform	.4	.4	2.5	1.9	5.2	.94
6 BDCM	.4	.2	1.7	1.3	3.6	.65
Mean %	14	6	46	34	100	100

It appears from the figures given in Table 4 that the main costs (80 %) are connected with the equipment, whereas the energy and hydrogen peroxyde expenses are in the range of 1 Nkr/m^3 (≈ \$·18/m^3). For a 95 % removal, the costs are from 40 % to several hundred per cent higher.

5. General Discussion

Laboratory experiments have suggested that organic matter in water is quantitatively converted to CO_2 and H_2O by UV radiation and hydrogen peroxide. For drinking water purposes this seems ideal: no foreign chemicals added and no residual-component problems! However, the present preliminary experiments suggest that the costs are high.

Nevertheless, the method should be further investigated. It is important to emphasize that the mechanisms behind this mineralization of aquatic organics are not clearly understood and that an increased efficiency may be achieved by a combined use of theoretical consideration and recent research and practical experiments.

We find it reasonable that the work is continued along the following lines, experimenting on:

1. Action of cataysts
2. Combination of chemicals
3. The most effective wave length
4. Increased efficiency of UV-lamp
5. Most effective way of dosing the active oxygen
6. Identification and biological evaluation of residuals

It has been stated that some reactive intermediates are involved which are formed by the action of light. Hydroxyl radicals are, as mentioned in the introduction, suggested as such an intermediate (7,10,11).

Zepp and coworkers (14) are using the term "singlet oxygen", stating that this may be generated in water by light energy and oxidize a variety of organic substances. They suggest, as Kautsky, that the most likely mechanism for the oxygenation in the environment is that light energy adsorbed by a sensitizer is transferred to ground-state oxygen to form singlet oxygen, which in turn reacts with the organic substance or "acceptor" to form a peroxide. In their experiments they demonstrate the importance of the presence of "singlet oxygen sensitizer". The results outlined above indicate a catalyzing or sensitizing action of some constituents in the humus sample, and a combination of chemicals may accelerate the mineralization processes.

In the work of Zepp and coworkers (14) the 366-nm line is used. In the work presented above, the UV source is a lamp which is claimed to have a sharp maximum at 254 nm. It is reasonable to assume that the wave length of the radiation will greatly influence the results. The UV-lamps commercially available have a relatively low effect. Those used in the present work are reported to give less than 25 % of the energy used. However, according to the manufacturer, this will be improved in the future.

The hydrogen peroxide is added to the test water immediately before the start of the experiment. It is interesting to note that the most effective H_2O_2-dose appears to be independent of the concentration of the organic matter present. The fate of the H_2O_2 added to the polluted water during the 2-4 hours lasting experiment is, however, not completely known. It is possible that the mineralizing effect may be improved by applying the active oxygen continuously or stepwise during the run.

The "ghost" behind drinking water and drinking water treatment today is the organic residuals. The engagement with regard to chlorination of water containing organics in general and humus in particular is considerable throughout the whole world. This concern about the residuals and their potential toxicity should also be applied to both natural and artificial UV radiation. In the present work some analyses on the residuals after UV-H_2O_2 treatment are in progress. At any rate, this type of research is essential in future work with this principle of drinking water treatment.

6. Conclusion

There is need for a method by which it is possible to eliminate organic matter from drinking water. Combined use of UV radiation and active oxygen appears in principle to be a promising method in this respect.

Experimental results from a relatively small UV radiation plant (necessary residence time 5-20 h/m^3) suggest that the price of this treatment is high. The mechanisms involved are, however, not completely understood and the efficiency of the method may be improved by altering the conditions, studying the effect

- at different wave lengths
- of a combination of chemicals
- of different ways of applying the H_2O_2 of modern UV-lamps and of different catalysts.

(1) ARMSTRONG, F.A.J., WILLIAMS, P.M., STRICKLAND J.D.H.
Photooxidation of Organic Matter in Sea Water by Ultraviolet Radiation, Analytical and Other Application
Nature 211 (1966), 5048, 481-483

(2) BEATTIE, J., BRICKER, C., GARVIN, D.
Photolytic Determination of Trace Amounts of Organic Materials in Water
Anal. Chem. 33 (1961), 1890-92

(3) GJESSING, E.T., SAMDAL, J.E.
Humic Substances in Water and the Effects of Impoundment
J. AWWA 60 (1968), 4, 451-454

(4) HENDERSEN, G.L., CROSBY, D.G.
Photodecomposition of Dieldrin Residuals in Water
Bull. Environ. Contam. Toxicol. 3 (1968), 131-134

(5) BULLER, C.D., EDGERLY, E. jr.
Photochemical Degradation of Refractory Organic Compounds
J. WPCF 40 (1968), 546-556

(6) MATSUURA, T., SMITH, J.M.
Photodecomposition Kinetics of Formic Acid in Aqueous Solution
AIChE J. 16 (1970), 1064-1071

(7) MATSUURA, T., SMITH, J.M.
Kinetics of Photodecomposition of Dodecyl Benzene Sulfonate
Ind. Eng. Chem.Fundam. 9 (1970), 252-260

(8) SCHORR, V., BOVAL, B., HANCIL, V., SMITH, J.M.
Photooxidation Kinetics of Organic Pollutants in Municipal Waste Water
Ind. Eng. Chem. Fundam. 10 (1971), 4, 509-515

(9) MAUK, C.E., PRENGLE, W.
Ozone with Ultraviolet Light Provides Improved Chemical Oxidation of Refractory Organics
Pollut. Engineer. 8 (1976), 42-43

(10) FOOTE, C.S.
Photosensitized Oxidation and Singlet Oxygen Consequences in Biological Systems
Free Radicals in Biology II, Academic Press, New York (1976), 85-133

(11) KOUBEK, E.
Oxidation of Refractory Organics in Aqueous Waste Streams by Hydrogen Peroxide and Ultraviolet Light
US Patent Nr. 4, 012, 321 (1977)

(12) SCHENK, G.O.
Institut für Strahlenchemie, Max Planck-Institut für Kohlenforschung, Mülheim, personal communication (1977)

(13) GJESSING, E.T.
Influence of Ultra-Violet Radiation on Aquatic Humus
Vatten 2 (1970), 144-145

(14) ZEPP, R.G., WOLFE, N.L., BAUGHMAN, G.L., HOLLIS, G.L.
Singlet Oxygen in Natural Waters
Nature 267 (1977), 421-423

ANODIC OXIDATION AS A PROCESS STEP IN THE TREATMENT OF BACTERIALLY CONTAMINATED WATER

N. Kirmaier

Extensive scientific studies in recent years have been able to demonstrate the effectiveness of the bacterial decontamination of water by anodic oxidation [1-3].

The original hopes of being able to use anodic oxidation specifically in electrosynthetic processes were disappointed in most cases on account of the formation of undesirable by-products. Nevertheless, there was a positive outcome for the treatment of water: microbial constituents and oxidizable chemical substances present in the water are oxidized unspecifically. In this way microorganisms are inactivated and the chemical loading of water is degraded.

The electrochemical action of anodic oxidation in water treatment can be arranged under two group headings:

a) the actual step-through reaction at the phase boundary between the electrode and the electrolyte,

b) the secondary reaction (due to reaction products) within the solution.

Since as far as we know cathodic reactions do not cause bacterial inactivation, and chemical reactions cannot be solely responsible for the inactivation performance of the anodic oxidation reaction cells, the actual oxidation of the bacterial substrate of microbes must take place on the electrode surface or on the boundary region of the anode. The basic course of the reaction can thus be described by the general equation:

$$\text{Ox (I)} + \text{Red (II)} \rightleftarrows \text{Red (I)} + \text{Ox (II)}$$

where Red (II) stands for an active bacterium and Red (I) for an inactivated bacterium [4].

If the bacterium were inactivated by active oxygen, the reaction would depend on processes of diffusion through the bacterial cell wall and on further partial steps of the reaction in the cytoplasm and the cell nucleus up to the oxidative attack on the DNA or on messenger RNA [4].

Studies were carried out with waters (mains water, surface water) contaminated with viruses and bacteria. Fig. 1 shows the inactivation dynamics for the polio virus in Munich mains water, and Fig. 2 the inactivation dynamics for the ECBO virus [5]. Only a relatively slight reduction of the infectiousness could be achieved at low current densities, while with current densities of over 5 mA/cm^2 a complete inactivation of the test viruses used is possible [5].

Other problem microorganisms (in concentrations of up to 10^6 cells/ml) (gram-negative bacilli, aerobic spore-formers, yeasts, mycelial fungi, and gram-positive cocci) can likewise be fully inactivated.

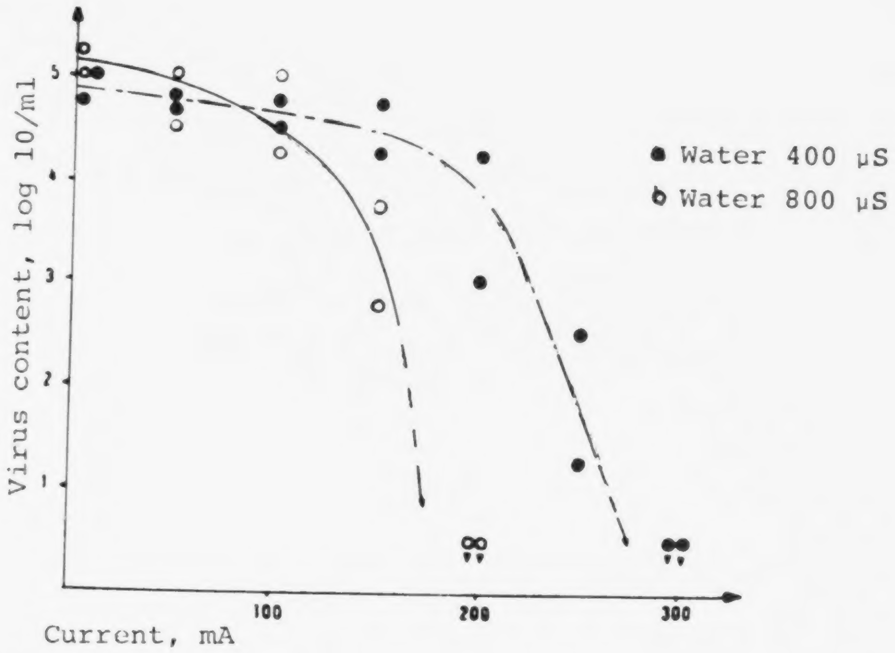


Fig. 1 Inactivation dynamics of the polio virus in Munich water, sterile filtration; through-flow 7.5 ml/sec at 10-12°C; conductivity adjusted with sodium chloride

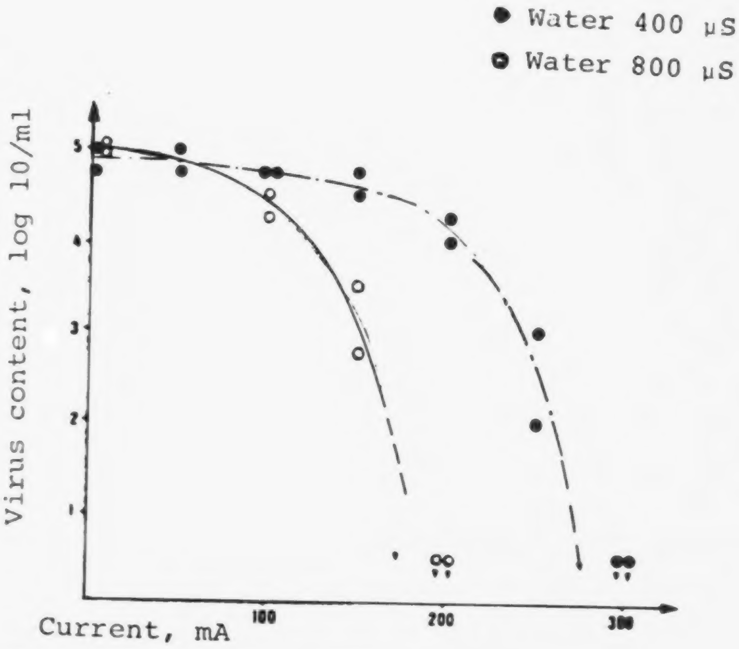


Fig. 2 Inactivation dynamics for the ECBO virus (5)

(1) Reis, A.
Die Anodische Oxidation als Inaktivator pathogener Substanzen und Prozesse
Klin. Wschr. (1951), 484

(2) REIS, A., KIRMAIER, N.
Anoden-Venturiscrubber zur Luftreinigung
G-I-T. Fachz. Lab. 22 (1978), 197

(3) REIS, A.
Ingenieuraufgaben in der Medizin
Biomed. Technik, Oldenbourg-Verlag, München/Wien
2. Aufl. (1977)

(4) EIBL, V.
Dissertation, TU München (in preparation)

(5) MAHNEL, H.
Virusinaktivierung in Wasser durch Anodische Oxidation
Zbl. Bakt. Hyg., Orig. B 166 (1978), 542

EXPERIENCE WITH POTASSIUM PERMANGANATE

K. Kötter

1. Preliminary remarks

When a conference considers the problem of oxidation processes and in so doing gives emphasis to chlorine and ozone, potassium permanganate should not be omitted from the discussion. This oxidizing agent undoubtedly does not rank among the primary agents used in water treatment, but it does have some interesting properties. Reference should therefore also be made to these, even though there are already detailed publications on potassium permanganate, on its chemical reactions, and on its possible uses in water treatment [1,2, etc.].

This short experience report will be limited to the use of potassium permanganate in recent years on Gelsen water. Before this, however, a brief mention of the commercial situation of potassium permanganate: a major manufacturer of this compound estimates that potassium permanganate is currently in use at more than 250 waterworks in North America and at more than 30 in Europe. For three years there has been a German Industrial Standard for this product in West Germany [3].

2. Use of potassium permanganate to prevent the growth of filamentous algae in infiltration reservoirs

The artificial enrichment of ground water with slow sand filtration with the use of large infiltration reservoirs is regarded as the principal process step in the Ruhr valley and in other large water treatment plants. Mass growth of algae and its adverse effects on this method of obtaining water and on the water quality have been known for a long time. In the spring the microscopic plankton algae predominate, in the summer it is the macroscopic filamentous algae

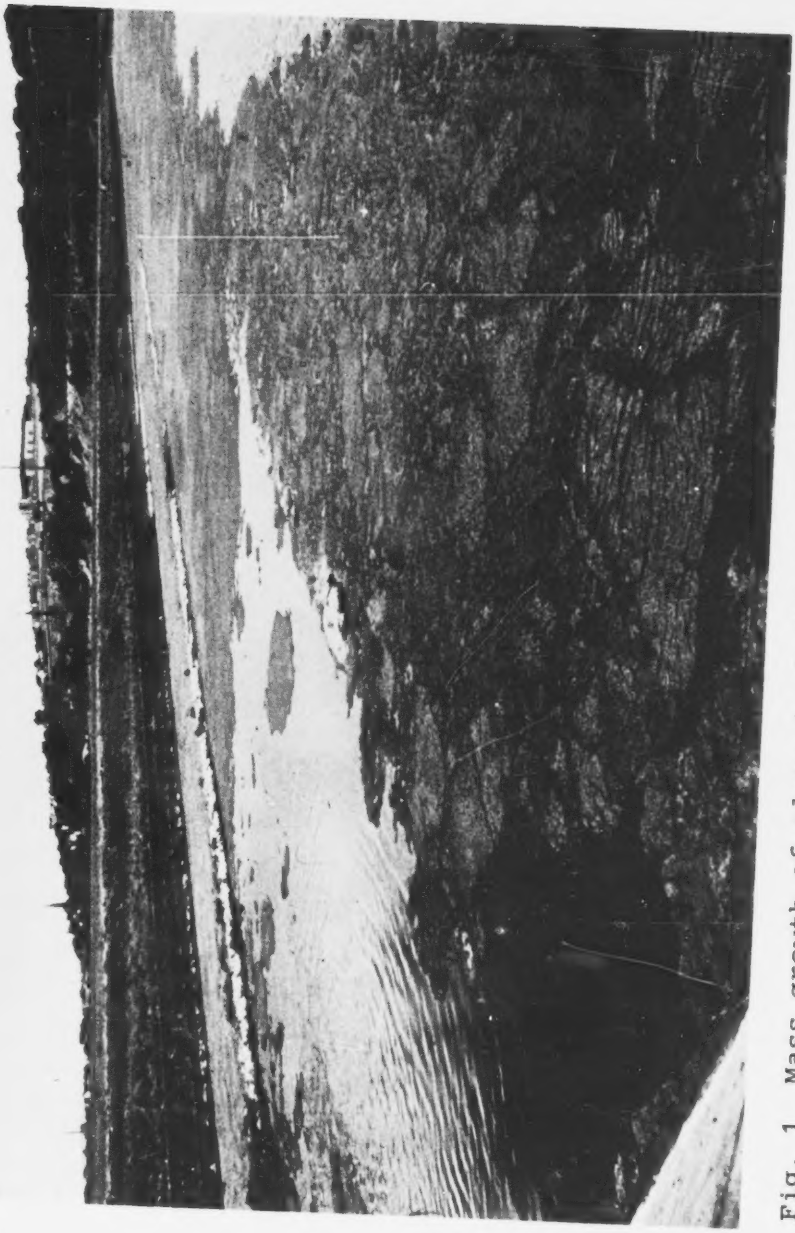


Fig. 1 Mass growth of algae in infiltration reservoirs

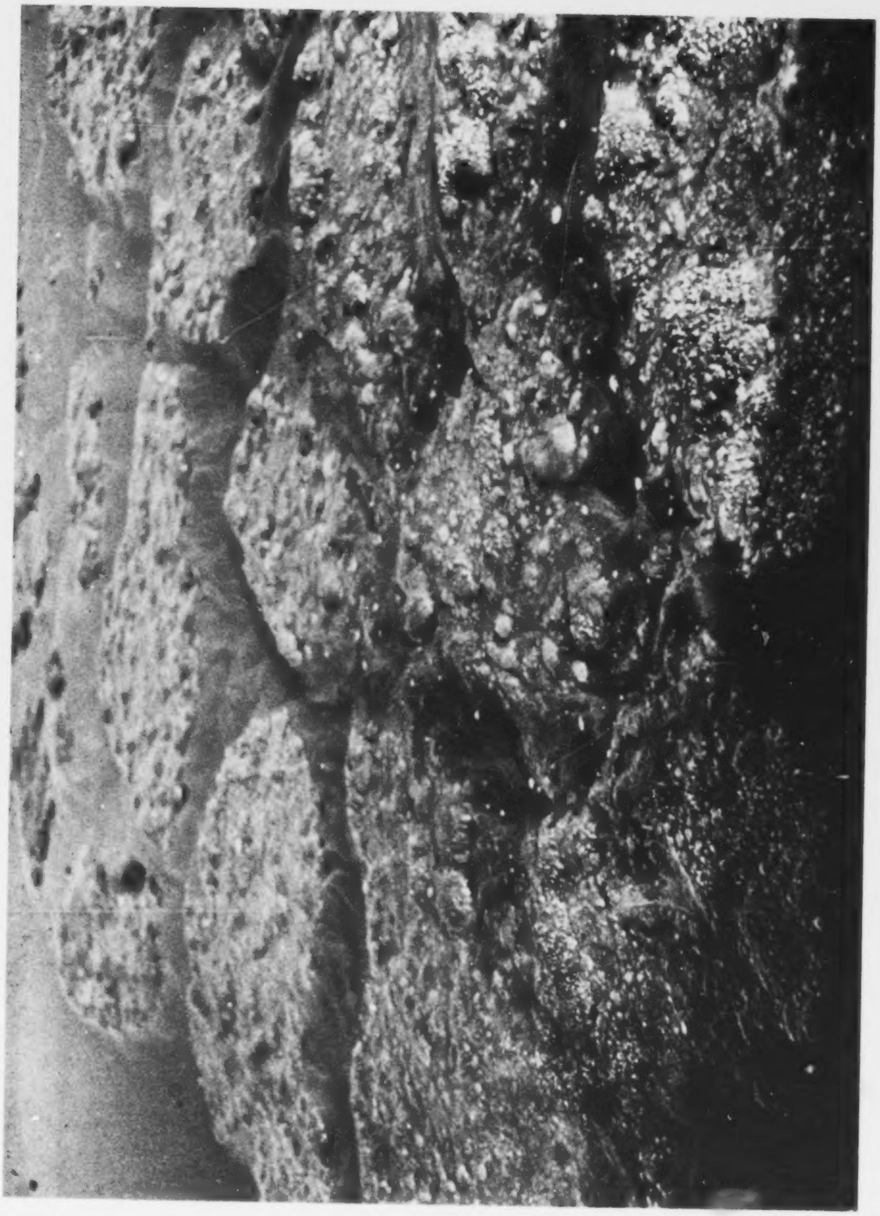


Fig. 2 Swimming filamentous algae as in Fig. 1, photographed from a closer distance

(Figs. 1 and 2). In the infiltration reservoirs the algae find conditions favourable for their proliferation, namely a slowing down of the flow rate, favourable illumination conditions, and a steady supply of food. Since the algae constantly release harmful metabolic products and on dying give off harmful incorporated substances, it is better to prevent the algal growth than to try and destroy it later, especially as relatively few chemical controlling agents are permissible in the treatment of drinking water.

The action of potassium permanganate on the growth of filamentous algae was studied at Gelsenwasser AG in large-scale trials lasting several years, performed in various water-treatment plants on the Ruhr and in reservoirs [4,5]. An addition of 1 to 1.5 g/m^3 of potassium permanganate to the inlets into the infiltration reservoirs largely prevents the growth of filamentous algae, while in a parallel trial with untreated tanks dense mats of Hydrodictyon were produced.

The action mechanisms of the potassium permanganate remain largely unexplained. They could be based on its oxidizing properties or on other properties toxic to the algae.

The considerable reduction of the water's transparency to light undoubtedly plays an important part. Certain wavelengths are absorbed to the extent of up to 99%. Therefore the light conditions at the bottom of the reservoir are no longer adequate for the development of the algae.

To stop the growth of filamentous algae the $KMnO_4$ addition must be commenced promptly in the spring. When already formed, algae swimming to the surface are little affected and can reproduce on the well illuminated surface of the water. In the light of the positive experience, potassium permanganate dosage plants have in the meantime been installed in all the Ruhr waterworks of Gelsenwasser AG, and since the spring of 1977, with the exception of some remotely situated reservoirs, all the artificially infiltrating water in these Ruhr waterworks has been first treated with potassium permanganate.

3. Action of potassium permanganate on plankton algae in infiltration reservoirs

The favourable action of potassium permanganate unfortunately extends only to the filamentous algae, and not to the plankton algae. This may be partly due to the fact that these algal forms develop in free water bulks, where because of the small layer thickness the light absorption of the permanganate has less effect than at the bottom of a reservoir.

In the summer of 1973 an attempt was made at Halingen waterworks to prevent the growth of plankton algae by increasing the amount of potassium permanganate added to 4 g/m^3. The treated water - in some reservoirs also receiving 0.3 to 0.6 g/m^3 of copper sulphate - assumed an intense violet coloration. Interestingly enough, these additions had no clearly positive or negative effects, either on the plankton algae or on the biological purification performance of the slow sand filter. Nor could any harm to the zooplankton be established.

On the over-all evaluation of potassium permanganate as an anti-algal agent in water treatment it must be said that it is sadly less effective against the plankton algae, i.e. against the algal species that at times impair the seepage. However, the filamentous algae, whose biomass production far outweighs that of the plankton algae and that can give rise to a considerable impairment of odour, can be controlled by potassium permanganate and so far no disadvantages of any kind have been discovered. This on the whole positive balance has lead to the decision to add potassium permanganate continuously to the raw water between March and September.

4. Potassium permanganate as an agent for the oxidation of dissolved manganese in an oxygen-containing water

The following partial report concerns the water treatment of the Stiepel waterworks of Wasserbeschaffung Mittlere Ruhr GmbH (WMR). The waterworks are situated in the Ruhr valley and are operated with Gelsen water. Up to 2500 m^3/h of true ground water and Ruhr bank filtrate are used. There is no artificial ground water enrichment via infiltration reservoirs or absorption wells. The manganese contents in the drinking water rose in the 'sixties to 5 - 8 mmole/m^3 (0.25 - 0.40 mg/l) of Mn, although the oxygen content in the natural ground water and ground water enriched by bank filtration, i.e. in the mixture of raw waters of different origins, never fell below 3 mg O_2/l. By shutting down the most severely affected wells a temporary slight improvement of the mixed water quality could be obtained, but this measure was not regarded as a satisfactory long-term solution. The only promising countermeasure was the erection and setting in operation of a demanganization plant.

In collaboration with drinking water treatment companies and with the Engler-Bunte Institute of Karlsruhe University, various treatment trials were carried out with the particular aim of clarifying whether a biological or autocatalytic manganese oxidation takes place in water containing sufficient oxygen or whether the use of oxidizing agents would be necessary. At first biological oxidation was favoured, because this had proved to be effective and reliable in the reservoirs used at the Haltern waterworks (up to 50 m/h filtration velocity and 10,000 m^3/h throughput). At the Stiepel waterworks, on the other hand, a filtration preceded by chemical oxidation gave better results. Surprisingly, potassium permanganate proved to be a more effective oxidizing agent than chlorine. For this reason, and because without preliminary chlorination the formation of organic chlorine compounds does not come into consideration, a plant for long-term potassium permanganate addition was set up and put into operation. The construction and the operating results are presented in Fig. 3 and in the following list:

$KMnO_4$ addition : a constant 0.5 g/m^3, i.e. referred to the fluctuating manganese concentration in the filter inflow 0.9 to 2.1 times the stoichiometric amount.

Filter bed : 70 cm of pumice, 2 - 3 mm, bulk density 350 kg/m^3

70 cm of activated carbon, 1.5 - 2 mm, bulk density 700 kg/m^3

70 cm of gravel, 0.7 - 1.2 mm, bulk density 1600 kg/m^3

Filter velocity : 25 m/h max.

Running times : about 7 days

Throughput/running time : about 2500 m^3/m^2

Manganese content : before the filter 2 - 6 $mmole/m^3$
Mn = 0.1 - 0.3 mg/l Mn

after the filter 0.0 - 0.6 $mmole/m^3$
Mn = 0.00 - 0.03 mg/l Mn

pH (corrected by additions of NaOH) : ground water 6.9
filter inflow 7.4
waterworks outlet 7.8

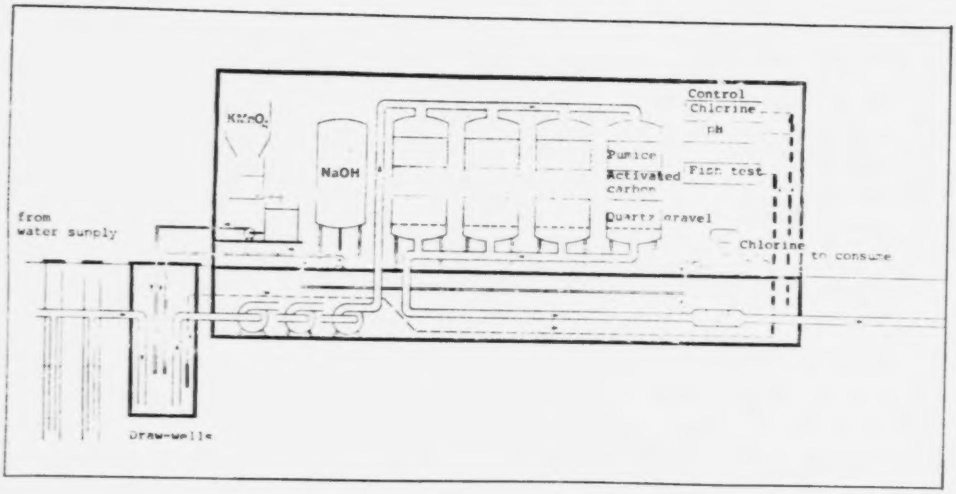


Fig. 3 Stiepel waterworks of the WMR, scheme of the treatment, metering of potassium permanganate into the draw-wells upstream of the filters

5. Oxidation of manganese in oxygen-free water

In contrast to the Ruhr bank filtrate, the Rhine bank filtrate coming from the gasworks and waterworks on the Lower Rhine is practically free from oxygen. The result is that in spite of its relatively high content of neutral salts it is only slightly corrosive. This situation would be changed if the freedom from oxygen were lost during the treatment. For this reason NGW did not make use of a biological or autocatalytic manganese oxidation in the process-technical design of the treatment plan for waterworks 1, and selected potassium permanganate as an oxidizing agent. The process scheme (see Fig. 4) has already been described by Heymann [6] at one of the earlier Karlsruhe conferences.

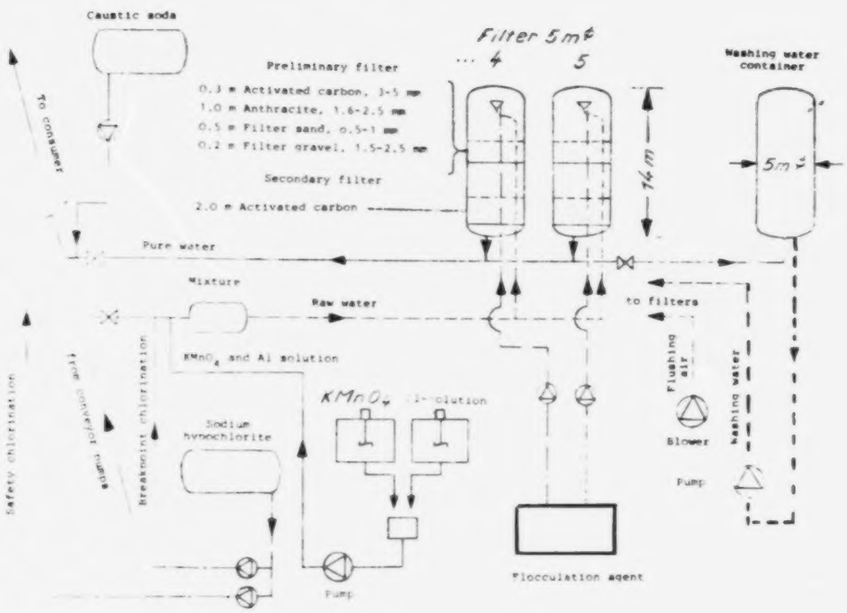


Fig. 4 Waterworks 1 of the NGW, scheme of the treatment, metering of potassium permanganate into the draw flow upstream of the filters

The potassium permanganate is added in proportional amounts to the raw water in the form of a 1% solution. The specific amount of potassium permanganate (in g/m^3) required is 2.1 times the weight concentration of the Mn^{2+}, i.e. the oxidizing agent is added in a slight excess over the stoichiometric amount. The flocculating action of the manganese hydroxide formed on organic water constituents is increased by the addition of aluminium chloride. After a residence time of 10 to 20 min the flocks produced are removed, following stabilization with a polymeric flocculation aid, through a three-layer filter. For the reduction of the excess permanganate ion the upper layer consists of activated carbon. This process removes iron and manganese ions to below the analytical detection levels.

Filtration of the water through a fibre-glass filter has been shown to be a simple check on the potassium permanganate dosage. The amount added is sufficient when a weak red coloration is discernible at a layer thickness of about 5 cm. Fully automatic regulation of the potassium permanganate addition is possible by continual measurements of the excess $KMnO_4$, but this is not necessary with the small changes in the concentrations of iron and manganese in the Rhine bank filtrate.

6. Further experiments on manganese oxidation

The Witten waterworks of Gelsenwasser AG are situated in the Ruhr valley about 8 km upstream of the Stiepel waterworks. The so-called pure water (up to 5000 m^3/h) obtained from below ground consists of small proportions of bank filtrate and true ground water, but mostly of artificially enriched ground water. It contains 1 - 2 $mmole/m^3$ = 0.05 - 0.10 mg/l of Mn. Because of the various origins of the manganese, only a partial load would be treated by demanganization of the raw water to be infiltrated.

Experimental treatments were performed following the prototype method of the Stiepel waterworks. These gave the surprising result that potassium permanganate, in spite of the physical proximity of the two waterworks and at first glance similar raw water situation, did not here give the same good results. Therefore, in the more recent large-scale plant the stronger oxidizing agent ozone is used. This example shows that potassium permanganate, despite its advantages from the economic and other points of view, is restricted in its uses and the limitations must be investigated in each individual case.

7. Disinfection of newly laid pipes with potassium permanganate

The disinfection of newly laid pipes is normally carried out with chlorine water in a concentration of about 50 g/m^3 Cl_2. In recent years various waterworks found that a single disinfection does not give the desired freedom from bacteria even with 24-h duration of action. This is particularly true for pipes with a high wall alkalinity (concrete pipes, pipes covered in cement mortar, pipes of asbestos cement, etc.), presumably because of the reduction in the bactericidal action of chlorine at higher pH.

Repeated high chlorination is a possible means -- though troublesome -- of avoiding this disadvantage. The DVGW pamphlet W 291 "Disinfection of Water Supply Plants" [7], in the light of the good experience particularly at the Hamburg waterworks [8], which were the first to practise this process on a large scale, contains the proposal to use potassium permanganate in a concentration of 5 - 10 g/m^3. At Gelsenwasser AG sodium hypochlorite and potassium permanganate have been used together for years to disinfect newly laid pipes. The disinfectant solution normally contains 45 g/m^3 of Cl_2 and 12 g/m^3 of $KMnO_4$.

Fig. 5 shows the dependence of the redox potential of various disinfectant solutions on the pH. Similar results were obtained earlier by Gras and Konrad [9]. If we start from the assumption that the redox potential is a measure of the bactericidal action of disinfectants not only at various concentrations of a particular disinfectant but also in a comparison of different disinfectants, the greater effectiveness of pure potassium permanganate in comparison with chlorine is not quite comprehensible, but that of the disinfectant mixture is easily interpreted.

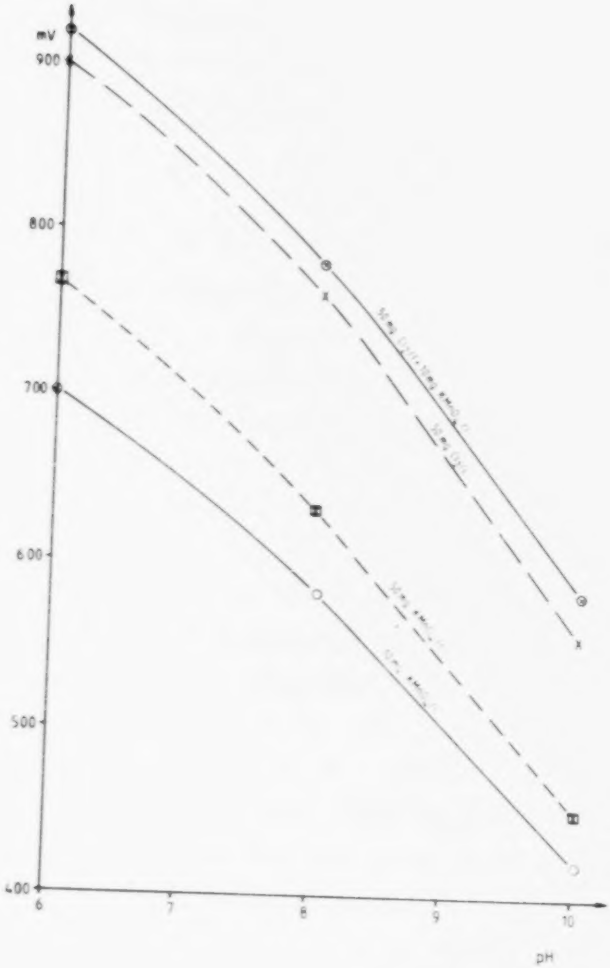


Fig. 5
Redox potential of various solutions of permanganate and/or chlorine, measured against an SCE in dependence on the pH

Under working conditions, the disinfectant mixture seems to lead to the desired freedom from bacteria more rapidly than pure chlorine. The only disadvantage is the greater expenditure in the preparation of the solution, but against this is the advantage of the coloration of the disinfectant solution in addition to the enhanced effectiveness already mentioned. During the addition flushing can take place at the hydrant until the red-violet solution appears, and with more recent rinsing analytical aids can be omitted. A visual check on disappearance of the disinfectant is sufficient.

Obviously it must first be checked whether a canalization or drainage is available, into which the solution of disinfectant containing the potassium permanganate can be harmlessly introduced.

8. Transportation and metering of potassium permanganate

Potassium permanganate is usually supplied in the solid form as a granulate in 50 kg drums. At the place of its use either a solution of constant concentration is prepared and metered out in liquid form (see, for example, Fig. 6) or a dry dosage is selected, regulated directly in accordance with the fluctuating volume flow of the water. All processes can be automated, and it is advantageous if the potassium permanganate granulate is "free running". A small addition of silicate base (according to the manufacturer's information) clearly reduces caking of the material, even at an elevated relative humidity.

When the potassium permanganate is used in larger quantities the necessary opening, emptying, and subsequent removal of the sheet-metal drums is a certain inconvenience. On the suggestion from Gelsenwasser one of the larger potassium

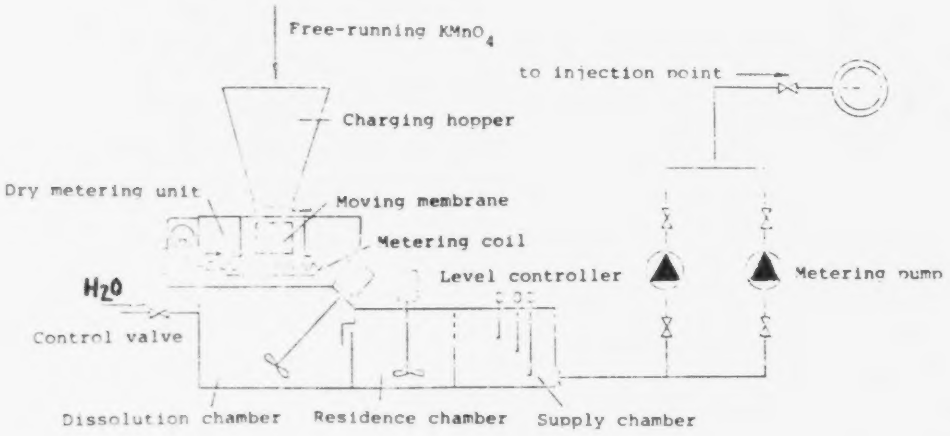


Fig. 6 Plant for the treatment and metering of potassium permanganate solution of constant concentration, schematic; after (2)

permanganate suppliers obtained in 1975 special permission from the Federal Transport Minister to transport the potassium permanganate on roads in stackable cubic containers (tank containers) of up to 1050-litre capacity. At the same time a filling installation for the tank containers was built at the manufacturers. In parallel with this, five metering stations of the kind shown in Fig. 7 were constructed at Gelsenwasser. By using refined alloy steel tank containers - shown in diagrammatic form - exchanged back and forth between the suppliers and the consumer, the use of potassium permanganate available in the solid form is substantially simplified.

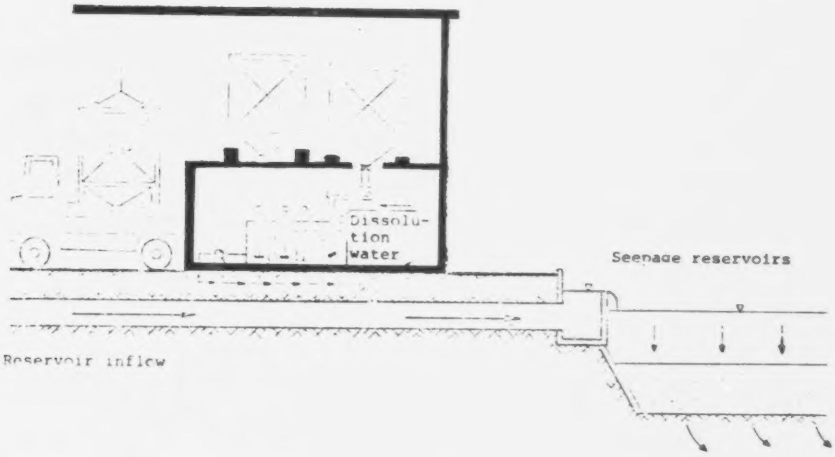


Fig. 7 Potassium permanganate metering station with delivery in containers, schematic

9. Summary

The present report of experience concerns the use of potassium permanganate in the Gelsenwasser group. While potassium permanganate is being replaced more and more in the laboratory as an analytical aid for the determination of oxidizability by stronger oxidizing agents, the technical product is used increasingly in water treatment. Potassium permanganate exhibits some characteristics, although sometimes in a weaker form, of properties and possibilities of use typical of the usual oxidizing, disinfectant, algicidal, and flocculating agents.

- As an oxidizing agent, its action on organic substances is weaker - but by the same token more sparing - than that of ozone and, unlike chlorine, it does not form reaction products that remain in the water.
- As a disinfectant it is suitable for the disinfection of plants but not for disinfecting drinking water at the end of the treatment.
- As an algicide it is effective within the described limits and has the particular advantage over other algicides of being permissible for the drinking water treatment of raw water.
- It may not be regarded as a flocculation agent in the true sense of the term, although small flocs with adsorbent and coagulating action are formed.
- Like some true flocculating agents, potassium permanganate is delivered in the solid form as a granulate and so requires a separate dissolution step. As with other flocculation agents, the flocs then formed must be removed in yet another process step.

Potassium permanganate is a chemical additive for water treatment processes which is used not in terms of individual strong actions but rather as a combination of several weaker actions.

(1) REIDIES, A.H., MACK, E.
Die Verwendung von Kaliumpermanganat in der Wasseraufbereitung in den USA
Vom Wasser 30 (1963), 81-103

(2) MACK, E.
Die Verwendung von Kaliumpermanganat in der Trinkwasseraufbereitung
Informationssschrift der Firma Th. Goldschmidt AG 6/73 (1973), 27, 2-23, siehe dort weitere Literatur

(3) DIN 19619 Kaliumpermanganat zur Wasseraufbereitung
Berlin, Beuth Verlag (1975)

(4) SCHMIDT, W.-D.
Probleme und Praxis bei der Algenbekämpfung in Infiltrationsbecken
Wasserfachl. Aussprachetagung 1972 Dortmund
Tagungsheft Frankfurt, ZfGW-Verlag (1972), 28-35

(5) PÄTSCH, B.
Maßnahmen zur Verhinderung übermäßigen Algenwachstums in den Wassergewinnungsanlagen der Gelsenwasser AG
Bericht "Ruhrwassergüte 1976" des Ruhrverbandes, Essen (1977)

(6) HEYMANN, E.
Erfahrungen bei der Anwendung einer Flockungsfiltration vor den Aktivkohlefiltern
Veröffentl. des Bereichs und des Lehrstuhls für Wasserchemie, Engler-Bunte-Institut der Universität Karlsruhe (1975), 9, 107-118

(7) DVGW-Arbeitsblatt W 291 Desinfektion von Wasserversorgungsanlagen, Frankfurt, ZfGW-Verlag (1973)

(8) GOLDA, W.
Desinfektion von Rohrleitungen und Trinkwasseraufbereitungsanlagen mit Kaliumpermanganat
Informationsschrift der Firma Th. Goldschmidt AG 6/73 (1973), 27, 34-35

(9) GRAS, KONRAD
Klärung der Oxidationskraft des Kaliumpermanganats in Abhängigkeit vom pH-Wert
Unveröffentl. Laborbericht 1972

THE USE OF HYDROGEN PEROXIDE IN WATER TREATMENT

H. Overath

1. Introduction

In many respects hydrogen peroxide invites application as a disinfectant and oxidizing agent in water technology:

- Hydrogen peroxide can be easily and exactly metered out in the liquid state.

- Hydrogen peroxide solutions between 35 - 50% are completely safe when handled correctly.

- Excess hydrogen peroxide can be removed quantitatively by activated carbon or by chlorine.

It is thus not surprising that hydrogen peroxide is from time to time considered as an alternative to chlorine and ozone. The following brief report attempts to clarify why hydrogen peroxide has not yet established itself, and what are the chances of its use in the future.

2. The most important chemical properties of hydrogen peroxide

Hydrogen peroxide has three important chemical properties:

a) It is an oxidizing agent

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2\ H_2O \qquad E_o = +\ 1.77\ V$$

$$H_2O_2 + 2e^- \longrightarrow 2\ OH^- \qquad E_o = +\ 0.88\ V$$

b) It is a reducing agent

$$H_2O_2 \longrightarrow 2\ H^+ + O_2 + 2e^- \qquad E_o = +\ 0.68\ V$$

c) It can decompose into oxygen and water in an intermolecular redox reaction

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2 + 46.9\ \text{kcal}$$

3. Examples of the application of hydrogen peroxide in the used water and waste water sectors.

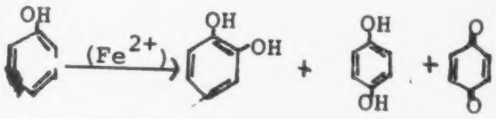
For some time now hydrogen peroxide has been used for the treatment of industrial waste waters whose components are toxic to activated sludge and which can be readily oxidized by it. Thus cyanide is oxidized to cyanate, nitrite to nitrate, formaldehyde to formic acid, and phenol - particularly in the presence of Fe^{2+} and Fe^{3+} ions - to the less toxic pyrocatechol, hydroquinone, and quinone (Table 1).

Since hydrogen peroxide can oxidize H_2S to elementary sulphur and thiols to dialkyldithiols, it has already been used for odour and corrosion control in the industrial and communal waste water sector (Table 1).

In highly charged waste waters hydrogen peroxide is able, as an oxygen donor, to maintain O_2 concentrations such as cannot be achieved on the basis of the entry values for atmospheric oxygen given by Fick's law. The same applies to the nitrification of discharges of two-stage clarification plants by filtration (Table 1).

While large doses of hydrogen peroxide can in many cases be used in industrial waste water treatment, only concentrations of 10 mg/l at the most are justified in the treatment of drinking water for hygienic and economic reasons. Since at this concentration it is second only to ozone in oxidizing strength, and it is known that on catalytic decomposition hydrogen peroxide can form very reactive intermediate products

Table 1 Use of H_2O_2 in the waste water sector

Function of the H_2O_2	Process	Reaction
H_2O_2 as an oxidizing agent	- Detoxification e.g. of	
	- cyanide	$CN^- \longrightarrow CNO^-$
	- nitrite	$NO_2 \longrightarrow NO_3^-$
	- formaldehyde	$HCHO \longrightarrow HCOOH$
	- phenol	
	- Corrosion and odour control	
	Oxidation of -SH	$H_2S \longrightarrow S_x$ $RSH \longrightarrow RSSR$
	- Inflated sludge control	unknown
H_2O_2 as an oxygen source	- Degradation of biologically oxidizable material (BOD)	aerobic biological (not chemical) oxidation
	- Nitrification in sand filters	aerobic biological oxidation of NH_3 by Nitrosomonas and Nitrobacter

of sufficient lifetime, decades of effort have been devoted to finding a suitable catalyst. The stimulus is always the hope that one's own work will be rewarded with the discovery of the "correct" catalyst. The magical intermediate products are called:

OH radicals and singlet oxygen.

These can both be formed from hydrogen peroxide and are extremely "fierce".

4. Formation of the OH radical from hydrogen peroxide

The decomposition of hydrogen peroxide is strongly exothermic, with an enthalpy change of $\Delta H = -22.62$ kcal/mole. Water and oxygen are formed as the final products:

$$(H_2O_2)_{dissolved} \rightleftharpoons (H_2O_2)_{liq.} + 1/2\ (O_2)_{gas}$$

It is assumed that the non-catalysed decomposition of hydrogen peroxide always proceeds via hydroxyl and perhydroxyl radicals in a non-chain reaction:

(1) $H_2O_2 \longrightarrow 2OH\cdot$

(2) $OH\cdot + H_2O_2 \longrightarrow H_2O + HOO\cdot$

(3a) $HOO\cdot + HOO\cdot \longrightarrow H_2O_2 + O_2$

(3b) $HOO\cdot + OH\cdot \longrightarrow H_2O + O_2$

The initial reaction (1) is rate-determining. Since the dissociation energy of the oxygen bond D(HO - OH) is 48.5 kcal/mole, it is not surprising that pure hydrogen peroxide decomposes at an immeasurably rapid rate.

The thermodynamic instability of the hydrogen peroxide in relation to its decomposition products H_2O and O_2, however, is manifested in the fact that its decomposition rate is accelerated catalytically by small quantities of a very large number of substances in the dissolved and solid state. Practically all types of dust and dirt, in particular certain heavy metal ions occurring in several valence states, and further more or less all vessel surfaces have this effect, various reaction mechanisms having been established for the homogeneous and heterogeneous catalysis.

If hydrogen peroxide is added to Rhine water, the natural concentration of potential catalysts is not sufficient for a rapid decomposition since, according to our measurements, the half-life amounts to a few days. An additional catalyst is required.

4.1. Production of OH radicals by catalysis with Fe^2

In most cases the catalyst recognized as the best is the Fe^{2+} ion. In combination with hydrogen peroxide, it is known as Fenton's reagent. The first hypothesis about the reaction mechanism was put forward in 1934 by F. Haber and J.Weiss [1]:

START (a) $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\cdot$

Unfortunately, in addition to the desired reaction with organic molecules, the OH radical formed can enter some other undesirable subsidiary and radical-capture reactions (Fig. 1).

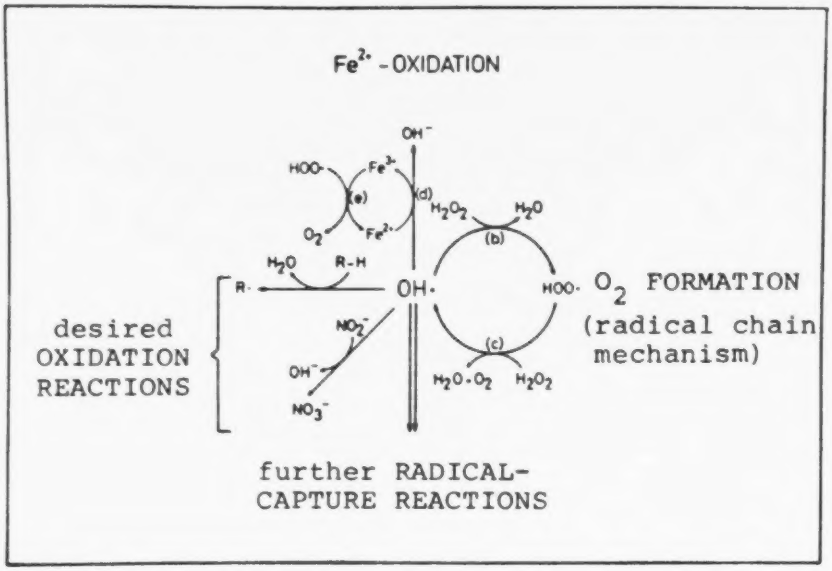


Fig. 1 Reactions of Fe^{2+}-catalysed H_2O_2

1. It can (again according to Haber and Weiss) function as a catalyst-independent chain carrier leading to O_2 formation:

(b) $OH\cdot + H_2O_2 \longrightarrow H_2O + HOO\cdot$

CHAIN

(c) $HOO\cdot + H_2O_2 \longrightarrow H_2O + O_2 + OH\cdot$

The new OH radical is formed at the expense of two hydrogen peroxide molecules. Although the intermediate perhydroxy radical can also react with organic molecules, it is essentially more critical in this reaction than the OH radical.

2. The OH radical can in addition oxidize Fe^{2+} ions:

(d) $Fe^{2+} + OH\cdot \longrightarrow Fe^{3+} + OH^-$

This route is not only undesirable as a radical-capture reaction but it also removes Fe^{2+} ions which are required for the initial reaction (a). Although, according to H.H. Baxendale [2], the Fe^{2+} can be reformed from Fe^{3+} ions

$$\text{(e)} \quad Fe^{3+} + HOO\cdot \longrightarrow Fe^{2+} + O_2 + H^+$$

this reaction is undesirable since the OH radical formation in accordance with reaction (c) is no longer possible. Moreover, the rate of this reaction is substantially smaller at pH 7 than that of the hydrolysis of the Fe^{3+} ions.

Finally there is

3. A number of other conceivable reactions, such as hydration, charge-transfer-complex formation, etc. that deactivate the OH radical and so remove it from the desired oxidative reaction.

In other words, the yields of OH radicals available for the oxidation are related to the hydrogen peroxide used, i.e. the $[OH\cdot]/[H_2O_2]$ ratio, considerably smaller than unity.

Fig. 2 shows the Fe^{2+}-catalysed reaction of hydrogen peroxide with ethanol, one of the closer-studied reactions with an organic compound. The H-abstraction by the OH radical takes place predominantly at the α-carbon. The oxidation to acetaldehyde and further to acetic acid takes place preferentially in the absence of atmospheric oxygen. If oxygen is present, the re-formation of the alcohol shown below plays a major role with the intermediate organic radical functioning as an electron carrier in the conversion of Fe^{2+} into Fe^{3+}.

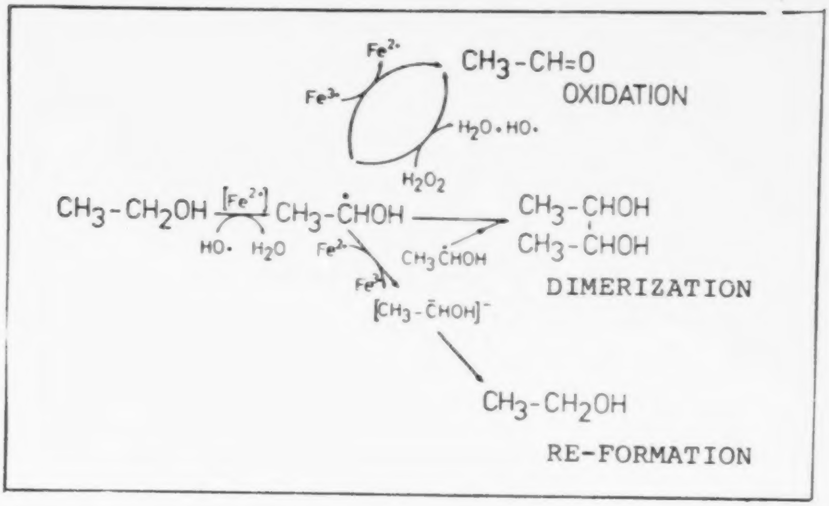


Fig. 2 Reactions of the OH radical with ethanol

It is therefore understandable that concentrated and acidified mixtures of hydrogen peroxide and $FeSO_4$ are used successfully for the quantitative ashing of foodstuffs. However, in the elimination of bacteria from drinking water the intensification of the bactericidal action of hydrogen peroxide by catalytic amounts of Fe^{2+} ions is less spectacular. Results from the Water Research Centre at Medmenham, England, substantially confirmed by studies in our laboratories in Wiesbaden in collaboration with the Degussa Company, show that even 120 mg of H_2O_2/l in 300 min destroy only 99% of E.coli. If in addition 2.8 mg Fe^{2+}/l and 0.05 mM of EDTA are added, the contact time necessary for this is reduced to 110 min [3,4]. The bactericidal action on the mesophilic and thermophilic bacteria in Rhine water was even worse (Fig. 3).

The preliminary results of our experiments on the use of hydrogen peroxide as an oxidizing agent in Rhine water are equally sketchy. Evaluation of the gas chromatogram with an ECD shows only relatively slight changes in the fingerprint.

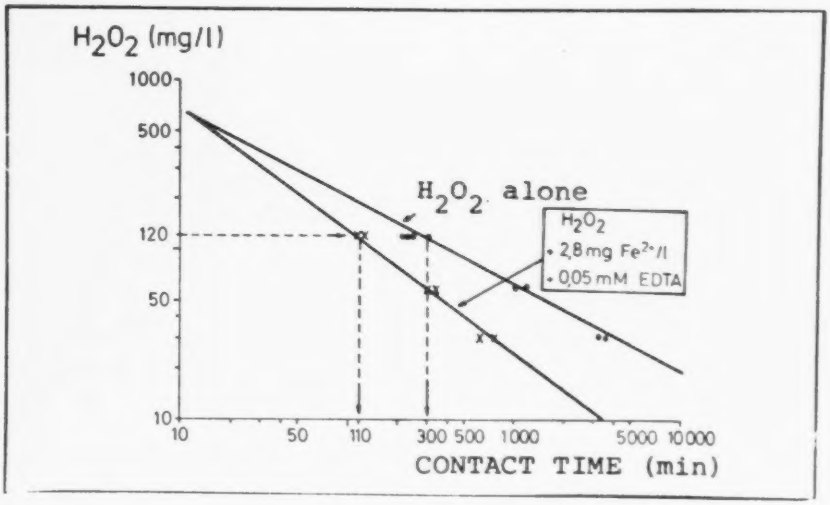


Fig. 3 H_2O_2 demand for 99% bacterial elimination (E.coli)

Only a few compounds, probably as a result of hydroxylation, had their boiling points raised. These phenomena should be investigated more fully in the future, extended to IR-spectrometric analyses, and compared with the action of ozone.

4.2. Production of OH radicals by photolysis

The production of OH radicals by photons in accordance with the reaction:

$$H_2O_2 \xrightarrow{hv} 2\ OH\cdot$$

has the advantage over the Fe^{2+}-generated OH radical synthesis

$$H_2O_2 + Fe^{2+} \longrightarrow OH\cdot + OH^- + Fe^{3+}$$

that two OH radicals are formed per hydrogen peroxide molecule. However the difficulty lies in the fact that, because of the large bond-dissociation energy of the O-O bond, only the shortwave UV-C region with wavelengths of 200-280 nm leads to usable radical yields. Therefore, at least in the raw water sector, all the absorption and control losses caused by pollution of the light-admitting surfaces will occur. However, in flocculated and filtered water the combined use of hydrogen peroxide with ultraviolet for the oxidation of organic constituents deserves more thorough study, all the more so since completely new antimony-doped mercury lamps emit ten times as much in the UV-C region as conventional mercury lamps and thus guarantee a high radical yield.

5. The formation of singlet oxygen from hydrogen peroxide

In addition to the OH radical singlet oxygen is a second very reactive particle that can be formed from hydrogen peroxide in a stoichiometric reaction with hypochlorite:

$$NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + {}^1O_2$$

The singlet oxygen is richer in energy by 22 kcal/mole than oxygen in its triplet ground state and its chemical behaviour is basically like that of an electrophilic olefin. It reacts:

a) as a highly reactive Diels-Alder component with conjugated diene systems,

b) in a (2 + 2) cycloaddition with electron-rich olefins,

and

c) in accordance with the general reaction type of the En reactions with olefins having an allyl hydrogen.

From these reaction types it can be seen that singlet oxygen - similarly to ozone - reacts essentially more selectively than the OH radical (Fig. 4).

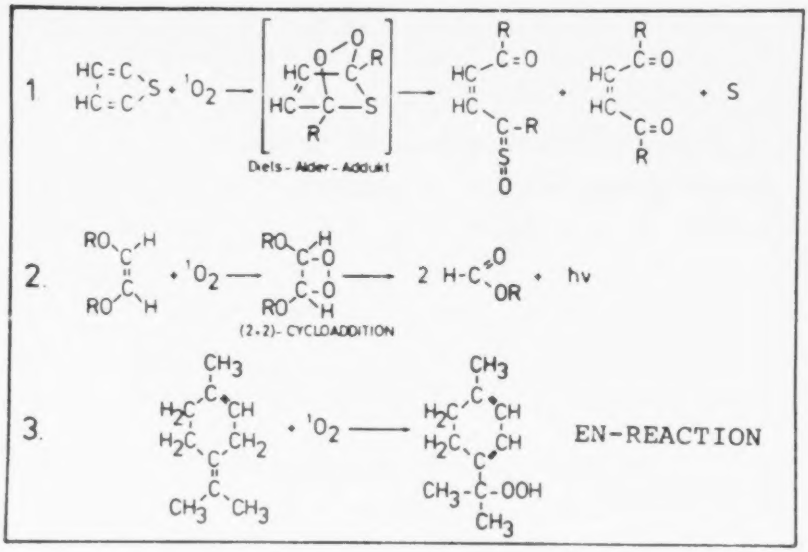


Fig. 4 Reaction types of singlet oxygen ($^1O_2$)

6. Summary and outlook

- Although hydrogen peroxide is highly unlikely to win a place as a primary disinfection agent, it promises in conjunction with low concentrations of other additives, such as NH_2Cl and Cu^{2+} ions, a good bacteriostatic action on water en route to the consumer.

- The oxidizing action exerted on organic water components by Fe^{2+}-catalysed hydrogen peroxide cannot compete with that of ozone. Nevertheless, there are hopes for its use, combined with UV, in water free from turbidity. Results similar to those in ozonization with subsequent activated carbon filters are conceivable in this sector.

- The replacement of potassium permanganate by hydrogen peroxide for demanganization has already been considered in connection with improving the operating time of the downstream filters.

- Hydrogen peroxide has up to now been used in drinking water technology but not as a supplier of oxygen. However, in the artificial enrichment of ground water it could serve as a source of oxygen and help to prevent the adverse consequences of oxygen consumption in the ground.

- In England a case is reported where hydrogen peroxide in backwashing water considerably prolonged the filter running times.

(1) HABER, F., WEISS, J.
Proc. Roy. Soc. A. 147 (1934), 332-351

(2) BAXENDALE, J.H.
Advances in Catalysis 4 (1952), 31

(3) -
An Investigation of Hydrogen Peroxide as a
Disinfectant of Potable Waters
Water Research Centre, Medmenham, England
Dez. (1974)

(4) OVERATH, H.
Versuche mit H_2O_2 und UV-Strahlen
ESWE-Bericht Nr. F 7/78

SOME ASPECTS OF THE USE OF CHLORINE OR CHLORINE DIOXIDE IN WATER TREATMENT

J. Valenta

The drinking water in the Zürich water supply obtained from Lake Zürich has been treated with chlorine for over 25 years. Chlorine is still used as the active agent in the preliminary chlorination, above all to protect the raw water plants against algae and DPP (Dreissena polymorpha Pallas) larvae.

Since 1971 chlorine dioxide has been used successfully as a mains-protecting agent. In the Zürich water supply system seven such ClO_2 plants are at present in operation.

Although the concentrations of trihalomethanes as a possible result of chlorinating drinking water should give no cause for concern, and although we still know relatively little about the possible reaction products associated with the use of chlorine dioxide, we are investigating the idea of replacing chlorine in the preliminary chlorination by chlorine dioxide. In connection with this, well-substantiated information on the effectiveness of chlorine dioxide on "Wandermuschel" larvae, and on the corresponding optimal dosage would naturally be important.

At Hardhof ground waterworks the bank filtrate is also to be treated with chlorine dioxide instead of chlorine before the inflow into the enrichment reservoirs. To this end the algicidal action of chlorine dioxide is currently being studied by the limnological division of the Zürich water supply.

Two further brief remarks may be made on the two oxidizing agents:

The first concerns the so-called "stabilized chlorine dioxide solutions." The subject was discussed 2 years ago at a conference in Zürich, and not much has changed in these 2 years. Such products are still offered to the drinking water works under various tradenames as a highly effective concentrate of chlorine dioxide which can be stored for at least one year without losing its effectiveness.

On the basis of several analyses in a number of Swiss and German laboratories, it can be stated that this product is a sodium chlorite solution, which must be regarded as impermissible for the treatment of drinking water. In order to determine the ClO_2 concentration, the suppliers prescribe only the usual iodometric analysis. In this method, the chlorite ion present is acidified and converted into chlorine dioxide, and then determined as such.

Finally, a remark on the analysis of the two oxidizing agents:

In spite of the ever-increasing number of instruments for checking the residual amounts of disinfectant by colorimetric, amperometric, or UV-photometric measurements, in many places simple manual methods are used for the same purpose with the aid of various comparators or simple portable colorimeters. For the determination of chlorine dioxide the colour disc or the chlorine scale is used practically without exception, and the value found is converted to ClO_2 with the aid of a factor. The problem now lies in the fact that, depending on which instructions are followed, this factor = 2 is sometimes used for multiplication and sometimes for division.

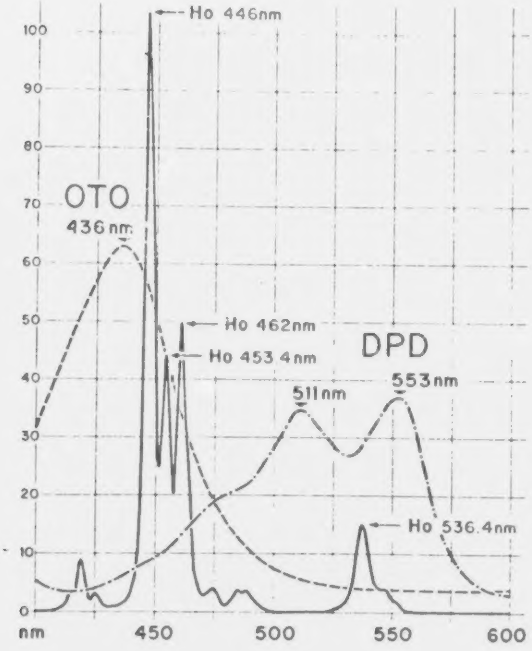
Our own measurements have confirmed the practically only 50% colouring action of chlorine dioxide in comparison with chlorine both with OTO and with DPD. We found the mean value for this factor to be 1.8, and the chlorine value must be multiplied by it.

Consider three figures on this subject:
Fig. 1 shows the simple absorption curves with OTO and DPD, with a maximum at 436 nm for OTO and two typical maxima at 511 nm and around 553 nm (about 7% higher) for DPD. In addition to this the figure shows the exactly defined maxima of the holmium calibration filter.

Fig. 2 shows the peak for chlorine, about twice as high as that for chlorine dioxide at the same concentrations.

The last figure shows the colour development curves for three commercial reagents between the first and the 26th minute. This slide also reveals the high instability of the colour with one of the two DPD reagents.

Such facts, perhaps banal at first sight can, however, have unpleasant and unexpected results when put into practice in various situations.



WV Zurich, August 1978

Fig. 1
Absorption curves of chlorine dioxide with OTO (---) and DPD (-•-•-) and of the holmium calibration filter

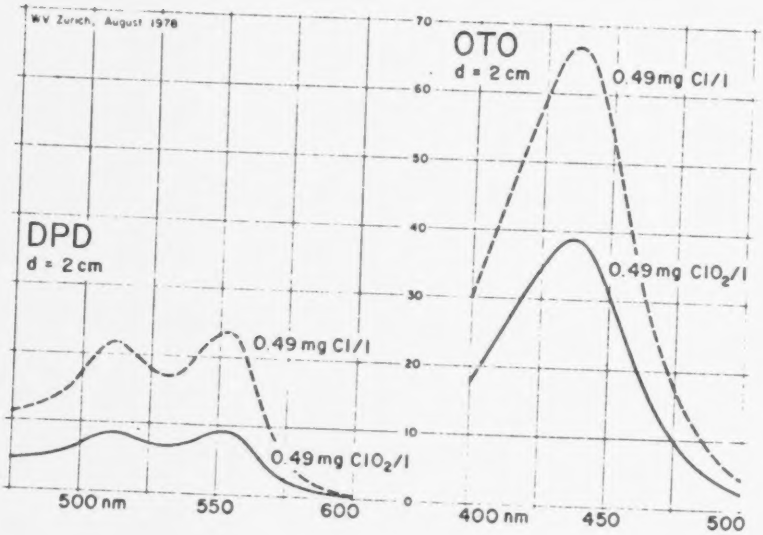


Fig. 2 Absorption curves of chlorine and chlorine dioxide in equal concentrations with OTO and DPD

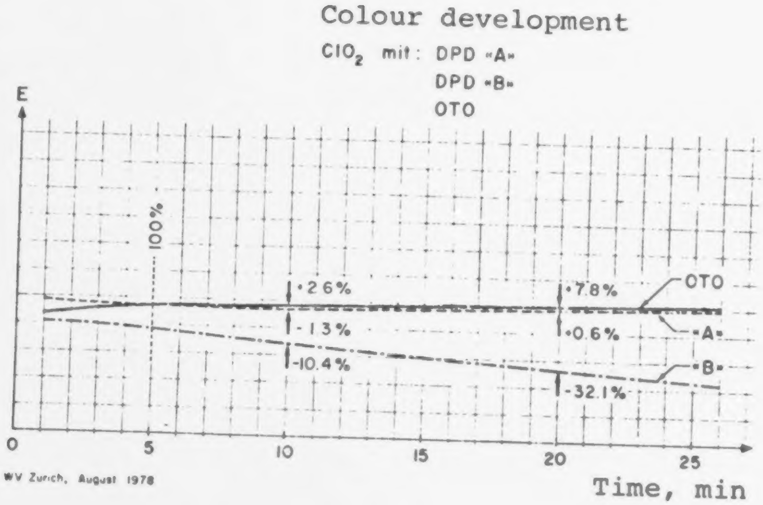


Fig. 3 Colour development curves of chlorine dioxide with various reagents

BIOLOGICAL METHODS FOR THE TREATMENT OF GROUND WATER

Y. Richard

I. INTRODUCTION

In recent years renewed interest has focussed upon ground water. For example, in the United States the production of water of subterranean origin has doubled in 20 years.

These waters are sought after for their organoleptic qualities and the theoretical absence of organic pollution. Nevertheless, their use sometimes entails considerable difficulties: bacterial proliferation in the distribution system, precipitation of iron or manganese compounds, and sulphurous or unpleasant odour - and these are only the most direct manifestations.

The cause of these various disadvantages must be sought in the very nature of ground waters, which are characterized by the absence of oxygen and which constitute a reducing medium. In waters of this kind one may find, depending on the composition of the surrounding soil, the various mineral species in their reduced form: divalent iron, ammonia, manganous ions, and hydrogen sulphide. All these elements are involved in well known biological cycles.

Ground water contains no organic carbon and does not permit the development of heterotrophic bacteria. In the reducing medium of ground water, in contrast, one finds a very small number of specific bacteria in a state of latent development. These are generally autotrophic with iron, manganese, or ammonia. It suffices for the medium to be very slightly aerated and set in motion, to create conditions favouring bacterial development and leading to a profound change in the quality of the water.

Biological treatment is nothing more than the understanding and control of this natural biological process, and the development of plant required to accelerate it and to deliver a water that will preserve all its organoleptic qualities.

Apart from the diversity of the mineral species involved (Fe, Mn, NH_3), we must also define the principal characteristics of biological treatment, while indicating the advantages and the disadvantages of such treatments.

It should be pointed out that a different form of pollution in ground water has been developing for some years. The form in question is nitrate pollution. This ion can be eliminated by biological means, using heterotrophic bacteria. However, this technique is rather similar to a reduction of nitrate nitrogen NO_3 to nitrogen N, and we shall not deal with this technique.

II. THE BIOLOGICAL PROCESS

In general, all biological treatments make use of autotrophic, or sometimes facultatively heterotrophic bacteria that use CO_2 and, for example, ammonia for their cellular development. These gain the required energy from redox reactions.

II.1. BIOLOGICAL DEFERRIZATION

This relies upon ferrobacteria, which have been studied in particular by Hasselbarth and Lüdemann (1). Many stations in Germany make use of the principle of biological deferrization.

In the list of bacteria drawn up by Starkay (2) (see Table 1) we find the following species: Leptothrix, Sphaerotilus, Crenothrix, and Galionella. When these bacteria undergo an autotrophic metabolism, they draw their energy from the exothermic reaction:

$$4Fe(HCO_3)_2 + O_2 + H_2O \longrightarrow 4Fe(OH)_3 + 8CO_2$$

TABLE 1 Various types of ferrobacteria (after Starkay, 1945, in the classification of Prevot, 1961)

Position in the classification	Species	Remarks
1. Sub-branch : Eubacteria		
1.1. Class : Asporulales		
1.1.1. Order : Bacteriales		
1.1.1.1. Family : Protobacteriaceae		
Genus : Thiobacillus	Th. ferro-oxydans	
2. Sub-branch : Algobacteria		
2.1. Class : Siderobacteriales		
2.1.1. Order : Chlamydobacteriales		filamentary, coated
2.1.1.1. Family : Chlamydobacteriaceae		
Genus : Sphaerotilus	S. natans	heterotrophic (problematic autotrophs)
	S. dichotoma	(or Cladothrix dichotoma)
	S. discophorus	(or Leptothrix discophora)
Leptothrix	L. ochracea	media poor in organic matter
	L. crassa	polluted media : heterotrophic
2.1.1.2. Family : Crenothricaceae		
Genus : Crenothrix	Cr. polyspora	facultative autotrophic
Clonothrix	Cl. ferruginea	
	Cl. fusca	
2.1.1.3. Family : Siderocapsaceae		
Genus : Siderocapsa	S. treubii	heterotrophic
	S. major	(problematic autotrophs)
Ferrobacillus	F. ferro-oxydans	
Sideromonas	S. confervarum	
2.1.2. Order : Caulobacteriales		pedicular
2.1.2.1. Family : Galionellaceae		
Genus : Galionella	G. ferruginea	strictly autotrophic
	G. major	media poor in organic matter

II.2. DEMANGANIZATION

Organisms that oxidize manganese have been studied by Schweisfurth (3) and by Mulder and Van Veen (4). They are listed in Table 2.

II.3. BIOLOGICAL NITRIFICATION

Nitrification reactions that oxidize ammonia to nitrate rely upon autotrophic bacteria. The nitrification process is divided into two stages, which bring into play two types of bacterial strains. This balance is described empirically by the following equations:

- Nitrite formation

During this phase the ammonia is oxidized to nitrite:

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \xrightarrow[\text{Nitrosomonas}]{} C_5H_7NO_2 + 54\ NO_2^- + 57\ H_2O + 104\ H_2CO_3$$

- Nitrate formation

The phase in which nitrites are oxidized to nitrates:

$$4\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- \xrightarrow[\text{Nitrobacter}]{} C_5H_7NO_2 + 3\ H_2O + 400\ NO_3^- + 195\ O_2$$

where $C_5H_7NO_2$ represents the chemical formula of the bacterial cell.

TABLE 2 Microorganisms capable of oxidizing manganese (after Mulder and Van Veen, 1963, and Schweisfurth, 1972)

A.	BACTERIA	
1.	Sub-branch Eubacteria	
1.1.	Class : Asporulales	
1.1.1.	Order : Bacteriales	
1.1.1.1.	Family : Pseudomonadaceae	
	Genuses : Pseudomonas :	Ps. manganoxydans
	Metallogenium	M. personatum M. symbioticum
2.	Sub-branch Algobacteria	
2.1.	Class : Siderobacteriales	
2.1.1.	Order : Chlamydobacteriales	
2.1.1.1.	Family : Chlamydobacteriaceae	
	Genuses : Leptothrix :	L. echinata L. lopholes
	Sphaerotilus :	S. discophorus (or Leptothrix discophora)
2.2.	Class : Thiobacteriales	
2.2.1.	Order : Hyphomicrobiales	
2.2.1.1.	Family : Hyphomicrobiaceae	
	Genus : Hyphomicrobium :	H. vulgare
3.	Sub-branch Mycobacteria	
3.1.	Class : Actinomycetales	
	Certain unidentified Actinomycetes.	
B.	PROTOZOA	
	Flagellae branch	
	Family : Monadaceae	Anthophysa vegetans (acc. to Pringsheim, 1966)
C.	ALGAE	
	An alga of the Diatomea class	(acc. to Peklo, 1909).

TABLE 3 Microorganisms capable of oxidizing ammonia

Microorganisms responsible for nitritation:

- Nitrosomonas europea and monocella
- Nitrococcus
- Nitrosospira
- Nitroscystro

N.B. Nitrosomonas is the most abundant, and its activity the greatest.

Microorganisms responsible for nitratation:

- Nitrobacter winogradskyi
- Nitrobacter agile
- Nitrocystro
- Bactodenna
- Microdenna

III. DEVELOPMENT CONDITIONS

Bacteria will only survive in a medium that conforms to certain conditions of pH, salinity, redox potential. The redox potential ranges vary appreciably according to the bacteria.

All the bacteria that affect the oxidation phenomena of ground water (iron, manganese, ammonia) develop in aerobic media and require the water to be aerated. Fig. 1 shows that the introduction of very small quantities of oxygen brings about a rapid increase in the redox potential. The introduction of $0.2\ mg \cdot \ell^{-1}$ produces a change of more than 250 mV in the water. However, variations in E_h are not always favourable to the development of all bacteria.

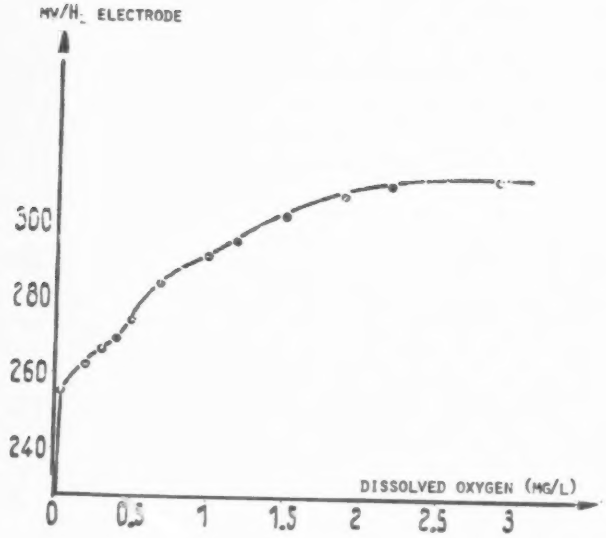


Fig. 1
Redox potential

For each type of bacteria we shall state the optimum redox potential conditions that favour their development.

III.1. DEFERRIZATION

Biological deferrization by ferrobacteria has been studied in particular by Hasselbarth and Lüdemann, 1971 and 1973, who quote very high passage velocities and retention capacities for filters working on this principle; many plants of this type are now in existence.

The pilot plant upon which we conducted tests is described in Fig. 2. The aeration system is designed to introduce only a limited amount of oxygen into the water (this being one of the main differences compared to the physico-chemical process). The results were as follows:

- Biological deferrization developed under the following conditions:

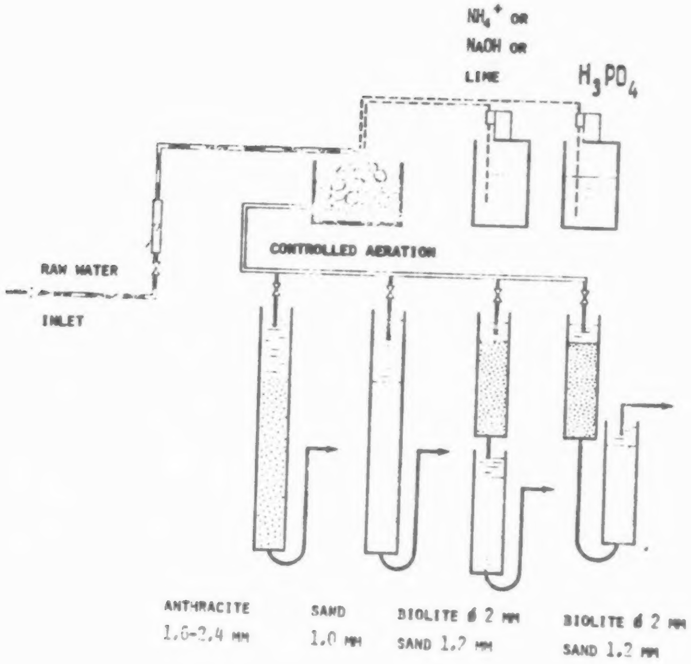


Fig. 2
Biological pilot plant

- dissolved oxygen concentration: 0.2 to 2 $g \cdot m^{-3}$
- pH: identical to that of the untreated water (6.3 - 6.4)
- redox potential: 40 to 200 mV on average
- rH: 14 to 20; if rH < 14, some Fe_{II} is left in the water. For a pH of 6.3 - 6.4 and a potential of 100 to 200 mV, biological deferrization takes place at the boundary between the Fe^{2+} and $Fe(OH)_3$ zones (see Fig. 3). Any excess oxygen will result in an increase of the redox potential.

  If, on the other hand, rH > 20 the filters are likely to become rapidly clogged since physico-chemical deferrization (with precipitation of amorphous floccular material) then competes with the activity of the ferrobacteria.

- There was no formation of a silica-iron complex.

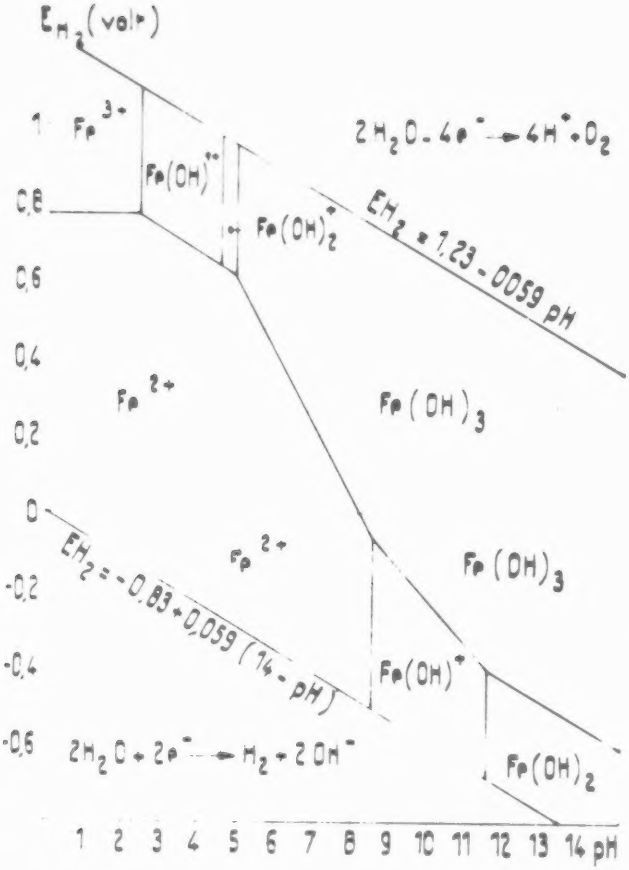


Fig. 3

Potential pH diagram for iron

III.2. NITRIFICATION

The curves of the redox potential as a function of the pH (see Fig. 4), show that nitrification takes place in potential regions higher than deferrization, between 300 and 500 mV. Nitrification is manifested in a fairly wide range of pH between 5 and 10, but the optimum pH range is about 8. The nitrification yields fall rapidly below pH 7.

Nitrification requires more oxygen than deferrization. 4.53 mg of oxygen are needed to transform 1 mg of ammoniacal nitrogen into nitrogen in the form of nitrate.

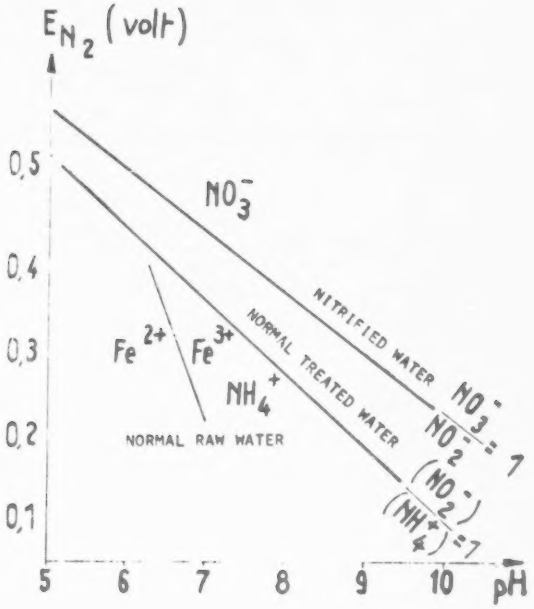


Fig. 4

Potential pH diagram for nitrification

III.3. DEMANGANIZATION

The results for manganese are less clear. Manganese can only precipitate in an alkaline medium (pH $\geq$ 9). Nevertheless, the redox diagram does not exclude chemical precipitation of manganese between pH 8.0 - 7.5 and at a redox potential between +400 and +500 mV. However, the reaction should be very slow.

The manganese bacteria can develop above pH 5.5 and the ground water must be aerated so as to give a redox potential between +100 and +200 mV if any biological oxidation of manganese is to be achieved.

III.4. SIMULTANEOUS ELIMINATION OF SEVERAL ELEMENTS

Manganese, iron, and ammonia are often found together in ground water at various concentrations; the concentration of the manganese is often the lowest. Are there specific conditions of redox potential and pH which permit elimination of all three elements, and if so, under what conditions? Several situations may be encountered.

a) Large amount of iron in the presence of ammonia and manganese

This case occurs frequently in ground waters. The introduction of very small amounts of oxygen, monitored by measuring the redox potential, enables biological elimination of the iron by filtration. The quantity of oxygen is always sufficient to eliminate traces of ammonia of the order of 0.2 to 0.5 $mg \cdot \ell^{-1}$ NH_4 either by nitrification or by bacterial assimilation.

Hasselbarth has observed bacterial elimination of manganese at the deferrization filter. This would be made possible by a very small addition of oxygen, to give the correct redox potential. Nevertheless, true manganese bacteria are not found in the filter (5).

In many cases iron is eliminated chemically in a first filter, and the biological elimination of manganese begins at the bottom of this filter and continues in a second filter (see Table 4).

b) Large amount of ammonia in the presence of iron and manganese

If the quantity of ammonia present in the untreated water is greater than 2.5 mg NH_4 per litre, the ammonia can be eliminated by means of an immersed filter packed with pozzolana, into which air is blown to satisfy the oxygen demand required for nitrification. The most favourable air/water ratios lie between 0.6 - 1.2. The ammonia is eliminated at the pozzolana filter. The redox potential of the water increases considerably with aeration, and deferrization is effected by chemical means.

TABLE 4 Deferrization in the presence of manganese and ammonia

	Rate m/h	Iron mg/l	Manganese mg/l	NH_4 mg/l
Raw water		5 - 15	0.3 - 2	0.1 - 0.3
Water F_I	10	0.1 - 1	0.1 - 0.5	0.05
Water F_{II}	10	0.01	0.01	0.05

- Aeration by spraying
- Reaction tank: 1 h

Filter I: sand depth 2 m
Filter II: sand depth 1.5 m

Duration of filtration cycles: F_I 48 h
F_{II} 1 week

The precipitation of ferric hydroxide leads to a reduction in the number of filtration cycles and entails frequent cleaning of the sand filter placed behind the pozzolana filter.

IV. KINETICS OF THE BIOLOGICAL PROCESSES

When the pH and redox potential conditions become favourable, the biological process is observed to develop very rapidly after an incubation phase that may be fairly long (from 3 days to 1 month).

The growth of the bacteria can be expressed by the following relationship:

$$\frac{dX}{dt}\,\frac{1}{X} = \mu - \sigma \qquad (1)$$

in which x = concentration of microorganisms ($mg \cdot \ell^{-1}$),
μ = specific reproduction rate of the bacteria (day^{-1})
σ = mortality rate of the bacteria (day^{-1}).

The specific reproduction rate of the bacteria depends on the concentration of the substrate S to be eliminated, in accordance with Monod's equation. In our case iron, manganese, and ammonia are designated by the letter S.

$$\mu = \mu_m \frac{S}{K_s + S} \qquad (2)$$

where μ_m = maximum specific reproduction rate (day^{-1}),
S = concentration of the mineral substrate to be eliminated ($mg \cdot \ell^{-1}$),
K_s = concentration of S when $\mu = \frac{\mu_m}{2}$.

Moreover, the elimination of the substrate is proportional to the concentration of bacteria present in the medium. We have:

$$-\frac{dS}{dt} = Y\,\frac{dX}{dt} \qquad (3)$$

where Y is the cell yield.

By substituting eqs. 1 and 2 into 3, we obtain the substrate elimination rate:

$$-\frac{dS}{dt} = \frac{\mu_m\, S}{Y\,(K_s + S)} - \frac{\sigma}{Y}\quad X \qquad (4)$$

If we put $\frac{\mu m}{\gamma} = \hat{q}$ and $\frac{\sigma}{\gamma} = K_d$, an endogenesis term, equation 4 becomes:

$$- \frac{dS}{dt} = \hat{q} \frac{S}{K_s + S} - K_d \quad X \qquad (5)$$

The importance of equation 5 is related to the kinetics of mineral substrate elimination, which govern the dimensioning of the water-treatment plant to be brought into operation.

In effect, the reaction order may vary according to the concentration of S to be eliminated. The K_s values of all the elements considered are small; for example, for ammonia K_s is less than 0.1 $mg \cdot \ell^{-1}$ of ammoniacal nitrogen and the value of K_s may be neglected in comparison with S. We shall assume that for the filtration rates used during the treatment of surface waters the distribution of the biomass is homogeneous in the filter. If $S \gg K_s$, equation 5 becomes:

$$- \frac{dS}{dt} = (\hat{q} - K_d) \quad X \qquad (6)$$

The elimination of S is independent of the concentration of S and the reaction order is zero with respect to S.

Integrating eq. 6 and putting $t = \frac{h}{U}$, where U is the mean filtration rate, we obtain

$$S_o - S = (\hat{q} - K_d) \frac{H}{U} \quad X \qquad (7)$$

Thus the S-elimination profile is linear (zero order).

If $S \leq K_s$, eq. 5 becomes:

$$- \frac{dS}{dt} = (\hat{q} \frac{S}{K_s} - K_d) \quad X \qquad (8)$$

The term $K_d K_s$ can be neglected, and integration gives:

$$S = S_o e^{-\frac{\hat{q}}{K_s} \cdot \frac{H}{U}} \qquad (9)$$

$$S = S_o e^{-\frac{\hat{q}}{K_s} \cdot \frac{H}{U}} \qquad (10)$$

In this case the S-elimination profile is an exponential decrease all along the filter (first order).

V. KINETIC REACTION ORDER AND PLANT OPERATION

Ground waters contain no suspended matter and it is necessary to reconstitute a water of comparable quality after the biological treatment, namely one possessing no suspended matter or turbidity. Because of this, the current practice is to develop the biological process within the body of the filter, since this makes it possible:

- to fix the bacteria to the filtration material and form an active biological membrane with a very large exchange area,
- to retain synthetic microorganisms and sludges
- to eliminate turbidity.

In such a case one may speak of biological filtration of the ground water. The treatment used should take into account:

- the biological growth factors set out above
- the filtration parameters.

The work of Devillers (6) and our own work on the elimination of ammonia (7) and the biological elimination of iron from well waters (9) have enabled us to write, in conformity with equation 7:

$$\Delta S = K\frac{H}{U}\,\theta^{(t - 10\,^{\circ}C)} \qquad (11)$$

where K depends on $(\hat{q} - K_d)\,X$ and on the size of the filtration material,

H = depth of the bed (in metres),

U = filtration rate ($m\cdot h^{-1}$),

θ = a value between 1 and 1.3.

This equation expresses the maximum quantity ΔS of substrate that can be eliminated by a filter of depth H, packed with a given filtration material and operating at a given rate. The ratio H/U is the apparent residence time of the water. Since the temperature of well waters is constant, and close to 12°C, it does not constitute a determinant factor.

In this case the elimination profiles of both ammonia and iron are linear (see Figs. 5 and 6).

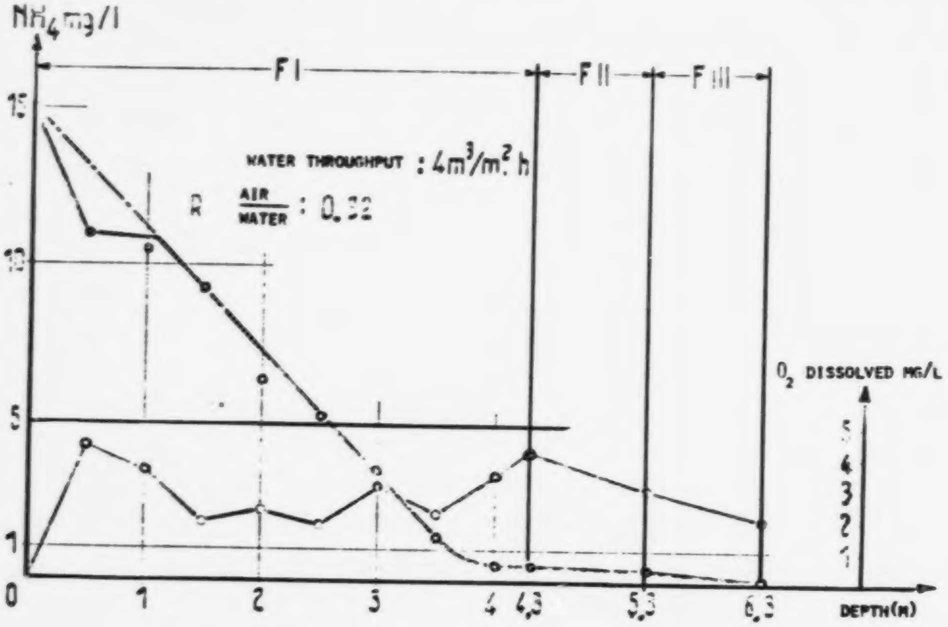


Fig. 5 Ammonia elimination profile

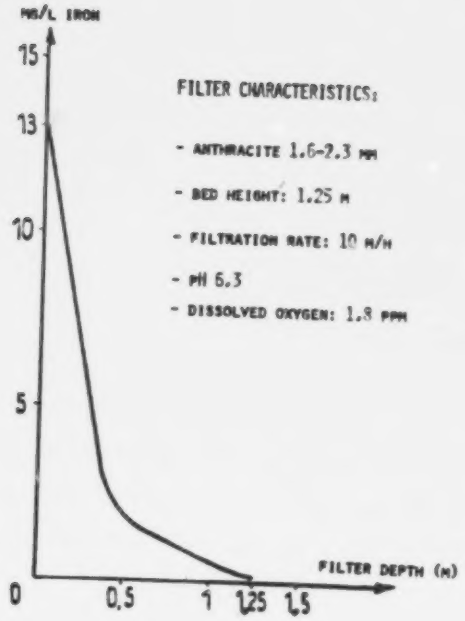


Fig. 6

Biological iron elimination profile

V.1. INFLUENCE OF THE FILTRATION RATE

Fig. 7 shows the influence of the water throughput on the quantity of ammonia eliminated by a filter 4 m in depth. The quantity eliminated decreases with increasing throughput.

While one can eliminate 12 $mg.\ell^{-1}$ of NH_4 at 4 $m\cdot h^{-1}$, the quantity of ammonia that can be eliminated falls to 3 $mg.\ell^{-1}$ to 20 $m\cdot h^{-1}$.

V.2. DISTRIBUTION OF THE BIOMASS

Equation 11 also shows that if one wants to eliminate large quantities of substrate,the residence time must be increased, either by increasing the depth of the filter bed or by lowering the water throughput.

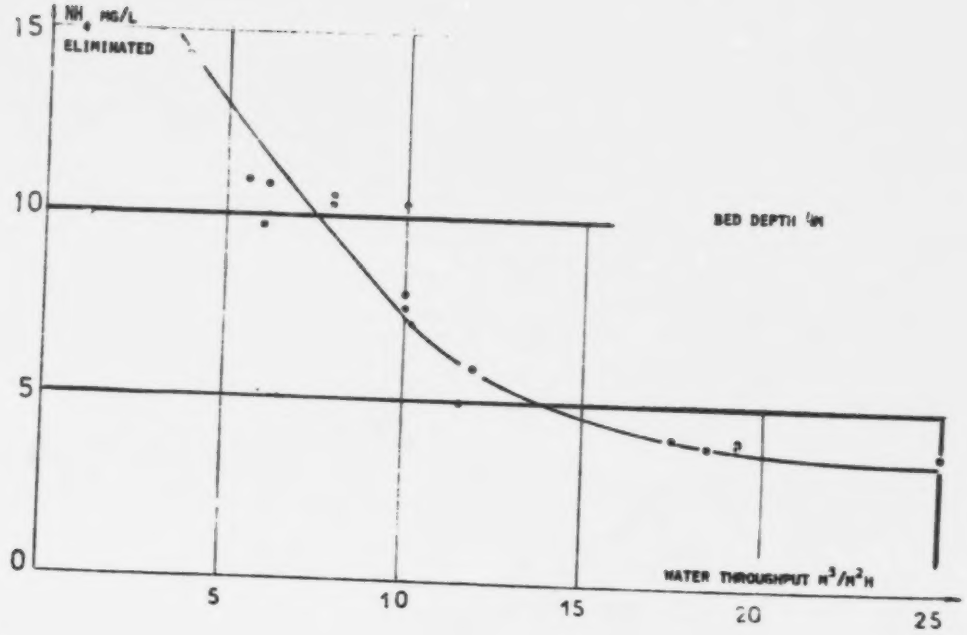


Fig. 7 Quantity of ammonia eliminated by an immersed filter, as a function of the water throughput

Experience shows that it is not advisable to reduce the water throughput too much, since the biomass will then be poorly distributed. ATP measurements along the filter show that its distribution along the filter follows the equation $X = X_o e^{-KH}$ (see Fig. 8), which results in a non-linear profile.

In this case, to eliminate the same quantity of the substrate ΔS, one must achieve a longer residence time and this again entails an increase in the bed depth, in contradiction to the objective sought initially.

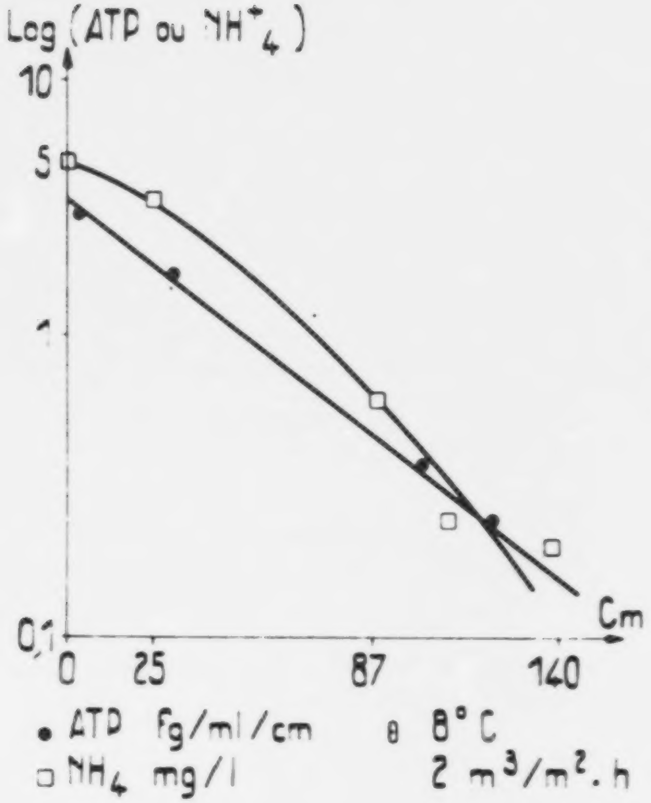


Fig. 8

ATP and ammonia profiles along a submerged bed

V.3. INFLUENCE OF THE LOADING S.

Equation 11 also shows that a biological filter eliminates a given quantity ΔS, and that if the loading S at the input to the filter is increased, the filter will still not eliminate any more than the amount ΔS in equation 11. Fig. 9 shows that when the NH_4 loading at the input increases from 2.5 to 6.5 $mg \cdot \ell^{-1}$, the filter continues to eliminate a constant amount of NH_4 (3 $mg \cdot \ell^{-1}$), so that the amount of NH_4 present in the effluent is increased (0 to 3.5 $mg \cdot \ell^{-1}$).

One must therefore take into account the nature of the boreholes and the future course of pollution when calculating the depth of the filters. A safety margin must be allowed for in case the loading S increases.

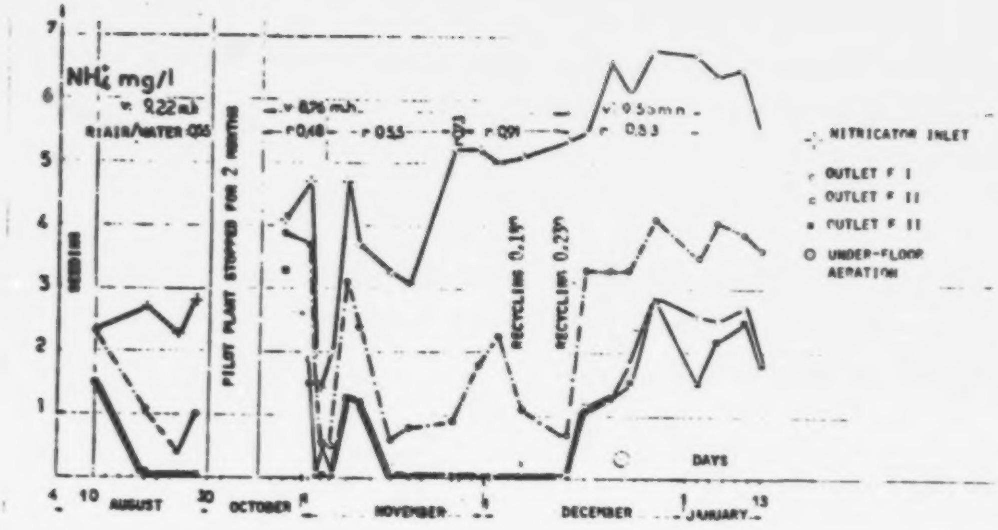


Fig. 9 Nitrification cycle
(pilot trial under pressure; bed packing depth 2 m)

The case when S is small:

Reaction 10 is applicable and shows that the elimination is of first order. This case corresponds to the elimination of trace amounts of NH_4.

It should be noted that, all other things being equal, a filter 4 m in depth will enable the ammonia content to change from 15 to 0.5 $mg \cdot \ell^{-1}$; to change from 0.5 to 0.05 $mg \cdot \ell^{-1}$ one would then have to add another 1.5 m of depth (giving a total depth of 5.5 m) - see Fig. 5.

V.4. INFLUENCE OF THE MATERIAL SIZE

The size of the materials used influences:

- the biological growth
- the filtration.

a) Biological growth

The biomass forms a biological film which grows around the material and develops an exchange area that will be the greater, the greater is the specific surface area expressed in $m^2 \cdot m^{-3}$. The finer the material, the higher the activity.

Fig. 10 shows the quantities of ammonia eliminated by two grades of pozzolana, one with a size between 3 and 5 mm and the other between 5 and 10 mm.

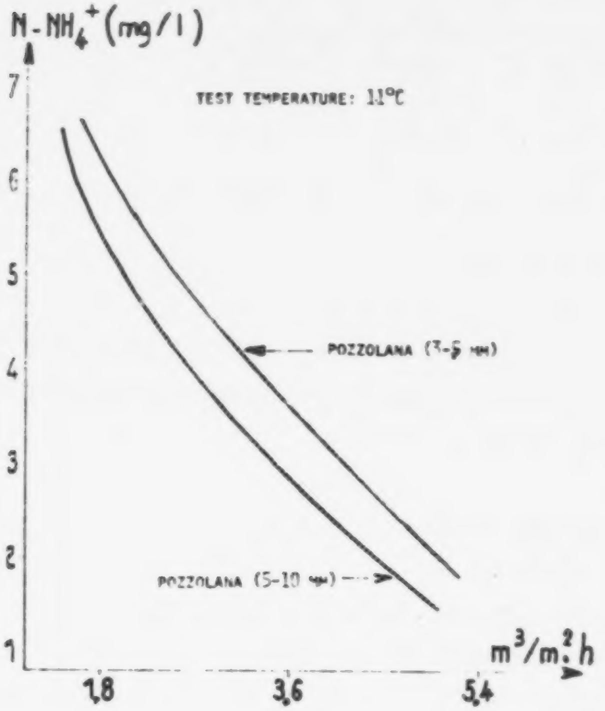


Fig. 10

Influence of material particle size on the quantity of ammonia eliminated in an immersed filter

b) Filtration

Can one, however, use finer and finer materials to improve the efficiency of the biological treatment?

In the case of classical filtration proceeding from the top downwards, and if we accept the Kozeny-Carman model, then for a filter of depth H packed with a material of specific surface area a the specific pressure drop may be written

$$\frac{\Delta P}{H} = K_{\eta} V a^2 \frac{(1 - \varepsilon)^2}{\varepsilon^3}$$

where η = viscosity of the water,
V = filtration rate,
a = specific surface area of the material,
ε = porosity,
H = depth of the filter bed.

We see that an increase in the specific surface area results in a very rapid increase in the initial specific pressure drop across the filter, and leads either to a reduction in the duration of the cycles or to the use of more powerful pumps.

This formula also shows that the pressure drop further depends on the porosity of the material, according to the factor: $\frac{(1 - \varepsilon)^2}{\varepsilon^3}$.

During the filtration cycle, the elimination of the Fe, Mn, or ammoniacal N is accompanied by a development of the biomass around the filtration material and the porosity decreases with time, causing the total pressure drop across the filter to become greater. Thus, the evolution of the pressure drop and the frequency of cleaning out the filter will be governed by the grain size of the material and the bacterial reproduction rate.

Influence of the reproduction rate on the frequency of cleaning out:

The reproduction rate μ can easily be related to the cell-division time, also known as the doubling time (t_d):

$$\mu = \frac{1}{X} \frac{dX}{dt} = \frac{d' \text{Log } S}{dt} = \frac{0,693}{t_d}$$

In the case of a filter operating correctly, where the concentration of Fe, Mn, or ammoniacal nitrogen at the filter inlet is constant and greater than K_s, the biomass grows exponentially according to:

$$X = Xo\ e^{\mu t}$$

The exponential growth of the biomass within a filter rapidly reduces the porosity and increases the pressure drop across the filter.

The bacterial reproduction rate varies from one species to another, and one finds different cleaning sequences in operation, depending on whether deferrization or nitrification is taking place.

- Nitrification:

Thus, according to the basic equations, the elimination of 20 $mg.\ell^{-1}$ of ammoniacal N will produce 3 $mg.\ell^{-1}$ of Nitrosomonas (10) and 0.5 $mg.\ell^{-1}$ of Nitrobacter. The elimination of 5 mg of ammoniacal nitrogen at 10 $m \cdot h^{-1}$ will produce 8 $g \cdot m^{-3}$ of sludge.

- Deferrization:

Our tests of biological deferrization enabled us to eliminate an average of 4000 g of iron per m^2 over 30 h at 10 $m \cdot h^{-1}$, or 133 $g \cdot m^{-2} \cdot h$ of iron. This iron accumulates within the filter in the form of a ferric sludge and the filter must be cleaned on average every 30 h.

A rapid calculation shows that the nitrification filter will in theory attain the same maximum permissible pressure drop in 20 days.

In fact, in the Paris region we have been using immersed filters for nitrification for 15 years, packed with pozzolana in the size range of 7 to 15 mm. The use of a coarser material limits filter cleansing to once a month. In the case of nitrification under pressure (1.2 bars), the filters needed no washing for a whole year.

V.5. INFLUENCE OF THE METHOD OF WASHING

For a biological filter to work well, the biomass must be in its exponential growth phase. In the event of major cleaning the biological activity of the filter is reduced.

The order of the reaction, which is 0 or ½ for optimum operation during most of the cycle, becomes 1 at the start of the cycle.

Excessive washing will remove a very large fraction of the biomass fixed to the filtration material, leaving behind a total initial biomass that is too small, and that must be regenerated at the start of the cycle.

In the case of biological deferrization, washing has a fundamental influence upon the filter-maturation time.

The best results have been obtained with:

- Blowing the sand with air only: 5 to 10 sec.

  This blowing allows elimination of old trichomes.

- Rinsing with water only, 100 $m \cdot h^{-1}$ - 3 min.

This rinsing causes a slight expansion of the material without impoverishing the biomass within the filter.

VI.6. CONCLUSION

An understanding of the biological factors that govern the biological processes makes it possible to eliminate undesirable elements such as iron, manganese, and ammonia by biological filtration.

The plant operation, packing depths, and the choice of the particle size of the filtration materials depend closely upon the element being removed and on the growth of the bacteria. These treatments can be relatively difficult to use unless the pH and redox potential conditions required of the bacteria are provided. The loading variations from different boreholes can give rise to poor elimination of the undesirable element, and it is necessary to include an aeration zone and a filtration zone.

(1) HÄSSELBARTH, U., LÜDEMANN, D.
Enteisenung und Entmanganung
Vom Wasser 38 (1971), 233-253

(2) STARKAY, R.L.
Transformation of Iron by Bacteria
J. AWWA 37 (1945), 963-984

(3) SCHWEISFURTH, R.
Manganoxydierende Mikroorganismen in Trinkwasserversorgungsanlagen
gwf-Wasser/Abwasser 113 (1972), 12, 562-572

(4) MULDER, van VEEN
Investigations on the Sphaerotilus Leptothrix group
J. Ant van Leenwenhook 29 (1963), 121-153

(5) HÄSSELBARTH, U., LÜDEMANN, D.
Removal of Iron and Manganese from Ground Waters by Micro-Organisms
Water Treatment and Examination 22 (1973), 1, 62-77

(6) DEVILLERS
Nitrification de l'eau: élimination de l'ammoniaque des eaux d'alimentation
T.S.M. L'EAU Oct. 1965

(7) BRENER, L., RICHARD, Y., MARTIN, G.
Elimination de l'ammoniaque des eaux de surface - Conférence prononcée au 58e congrès de l'A.G.H.T.M.
Bordeaux (1978)

(8) MOUCHET, P., MAGNIN, J.
Un cas complexe de déferrisation d'une eau souterraine
58e congrès de l'A.G.H.T.M., Bordeaux (1978)

(9) RICHARD, Y., BRENER, L., MARTIN, G., LEBLANC, C.
Study of the nitrification of surface water
I.A.W.P.R. 9th International Conference

(10) HAUG, R., McCARTY, P.L.
J. WPCF 44 (1972), 11, 2086

BIOLOGICAL REMOVAL OF AMMONIA

J.B. Goodall

Introduction

Pilot scale studies to evaluate cost and efficiency of ammonia removal from River Thames water by biological sedimentation (fluidised bed), biological filtration, and air stripping, were carried out between 1971 and 1975 at the Medmenham Laboratory of the Water Research Centre (1).

The early work quickly revealed that biological sedimentation was both technically and economically the best of the three processes and so the work was extended with the specific aim of being able to advise on the design of full scale plant (2).

This paper describes the biological sedimentation process and gives brief comparative details of the other two processes.

All the work was financed by the Directorate General, Water Engineering, of the Department of the Environment.

The ammonia problem

When ammonia is found in surface waters it is always as a result of pollution, usually from the excretions of wild and farm animals and sometimes from untreated or imperfectly treated sewage or leakage from sewers, cesspits, and septic tanks.

Ammonia is occasionally found in groundwaters as a result of biological denitrification or from the breakdown of protein by saprophytic bacteria and fungi.

It is believed that ammonia in drinking water does not present any direct health hazard and it is interesting to note that from many samples of water from distribution mains analysed at Water Research Centre there has been little or no evidence of oxidation of ammonia to nitrite or nitrate. Work in the Netherlands has shown, however, that levels of ammonia in excess of 0.3 mg/l as N can lead to aftergrowths in the distribution system and associated taste problems. Ammonia is toxic to fish,and ammonia removal may become an important aspect of fish farming, particularly where water is recycled.

There is no doubt that ammonia interferes with chlorination although the hazards of poor disinfection have been exaggerated in the past. The real disadvantage is the cost of the large chlorine dose required to oxidise ammonia and the difficulty of controlling the dose when the ammonia concentration varies. Increased chlorine dose can also presumably increase trihalomethane formation.

World Health Organization (WHO) European standards recommended a level of not more than 0.05 mg/litre in supply.

Non-biological ammonia removal processes

Air stripping

In this method the nitrogenous material is removed from the water - not merely converted into a different chemical state. This advantage must be offset against the possibility that ammonia gas discharged to atmosphere may cause air pollution or even re-dissolve in open water.

As ammonia is extremely soluble a high air to water ratio is required for efficient stripping. pH is also important, high values giving best results because only gaseous ammonia can be removed by air stripping and it is necessary to hold the pH between 10 and 11 to get 90% of dissolved ammonia in the gaseous form.

Experimental work

The experimental work was carried out in two rectangular mild steel towers each of 0.58 m^2 area and containing 2.1 m depth of 10 x 50 mm serrated wooden slats (Fig. 1). Water entered the towers through distributors at the top and air was supplied from centrifugal fans at the base.

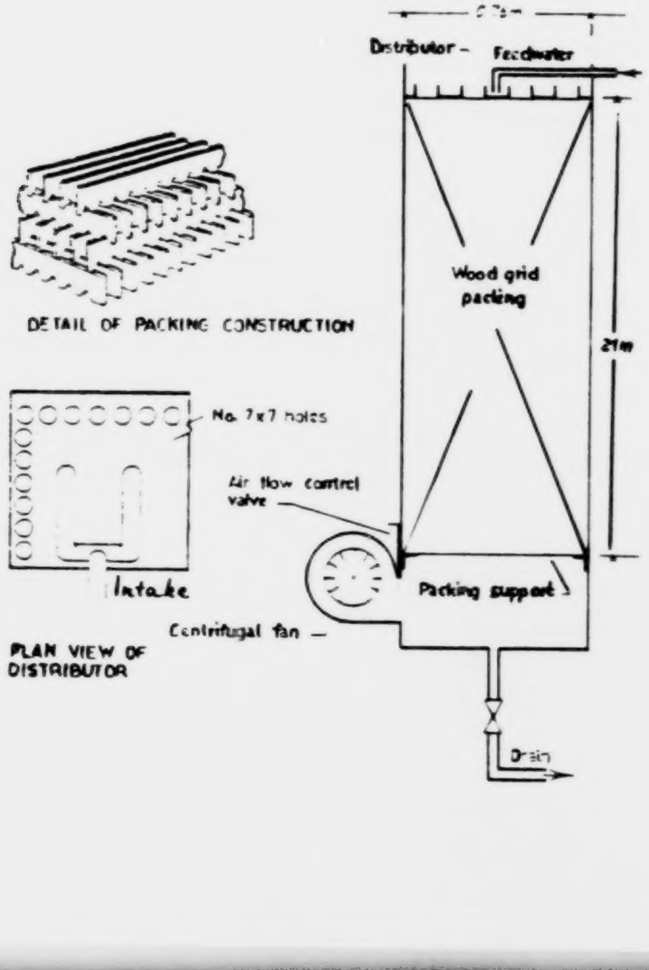


Fig. 1

Air stripping tower

The best result consistently obtained was 90% removal at pH 11 with a water to air ratio in the range 0.12 to 0.16 by weight.

Operating problems

There are potential operating problems in the air stripping of ammonia.

1. Ice formation from evaporative cooling in cold weather.
2. Calcium salt precipitation from CO_2 stripping.
3. Temperature effect - efficiency reduces with falling water temperature (Fig. 2) and reduced air temperature also affects the process adversely.

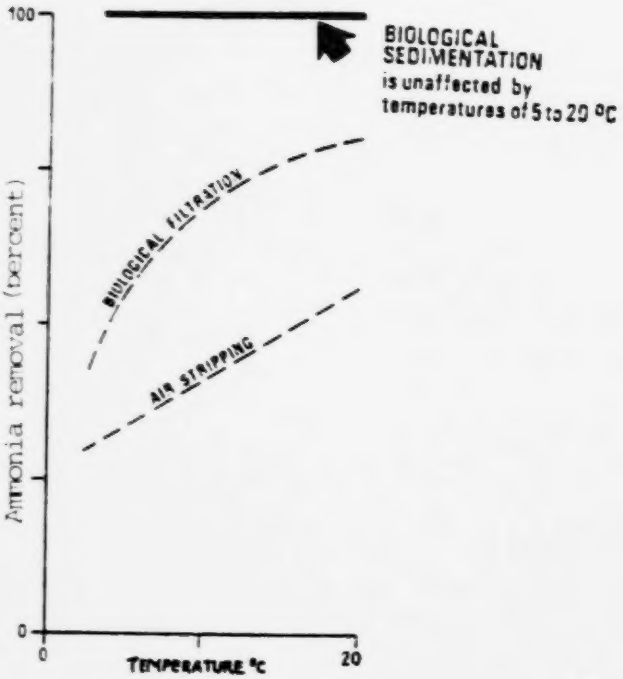
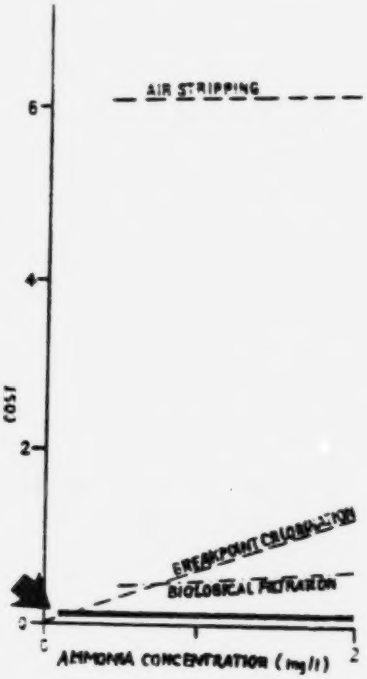


Fig. 2

Effects of water temperature

Cost

The cost of air stripping will always be much higher than that of biological processes (Fig. 3). The major cost is running the air blower but the cost of pH adjustment may vary widely depending on the buffering capacity of the raw water. Air and water temperature has a big effect on cost - it has been claimed, for example, that both capital and operating costs of air stripping would be three times higher in Sweden than in California (3).



Cost

BIOLOGICAL SEDIMENTATION
is the cheapest by far - even for ammonia concentrations as low as 0·1 to 0·2mgN/litre

Fig. 3

Comparative costs

Breakpoint chlorination

Ammonia is converted to chloramines. Conversion to trichloramine requires a chlorine dose about 8 1/2 times the ammonia concentration in addition to the dose required for disinfection. The method has the disadvantage of increasing the chloride content of the treated water and control can be difficult if the ammonia concentrations vary widely. High chlorine doses could presumably increase trihalomethane formation.

Breakpoint chlorination is worth considering at very low ammonia concentrations or following biological sedimentation when the dissolved oxygen content of the raw water limits biological removal. (See later). Breakpoint chlorination can be used under these circumstances to remove any small excess passing through the biological sedimentation unit.

Electrochemical removal (electro-oxidation)

It has been demonstrated that it is possible to convert ammonia in sewage directly to nitrogen gas at the anode of an electrolytic cell, but high efficiency is only possible if very expensive platinum electrodes are used (4). Fouling and corrosion would probably have a considerable adverse effect on cost.

Biological ammonia removal processes

Biological filtration

Pilot plant experiments were carried out using two 0.75 m diameter spun concrete pipes containing 2 metres depth of 20 to 40 mm graded washed shingle (Fig. 4).

The best ammonia removal achieved was 92.5% at a superficial velocity of 0.8 m/hr but increasing the treatment rate gave lower removal efficiencies with only 47% removal at 2.8 m/hr (Fig. 5). Temperature had a big effect on removal efficiency which was approximately linear between 6 and 12°C. At a nominal feedwater concentration of 3 mg/l N, 75% removal at 12°C declined to 51% removal at 6°C.

Analysis showed that ammonia was essentially converted to nitrate.

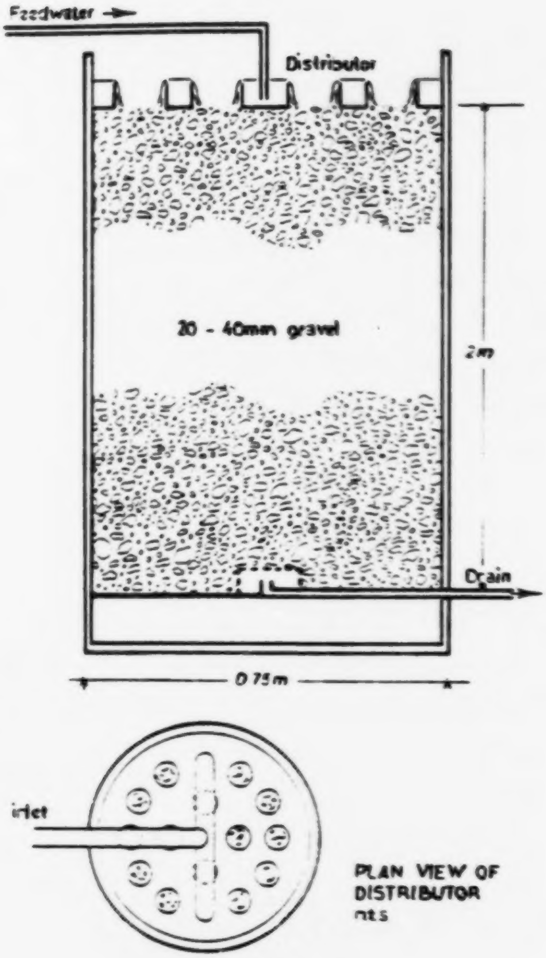
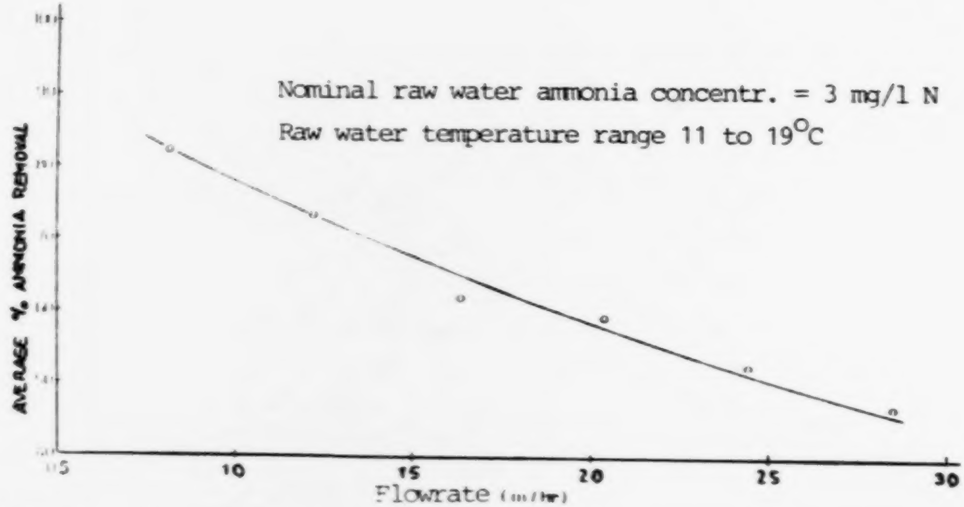


Fig. 4

Biological filter construction



Nominal raw water ammonia concentr. = 3 mg/l N

Raw water temperature range 11 to 19°C

Fig. 5 Effect of flowrate on biological filter performance

Biological sedimentation

The experimental work was done in two mild steel, square section tanks 4 metres high and of 0.58 m^2 area. Raw water entered through a pipe directed downward into the tapered bottom and flowed upwards to be removed by launders at the top (Fig. 6). The initial ammonia concentration in the raw water was 3 mg/l.

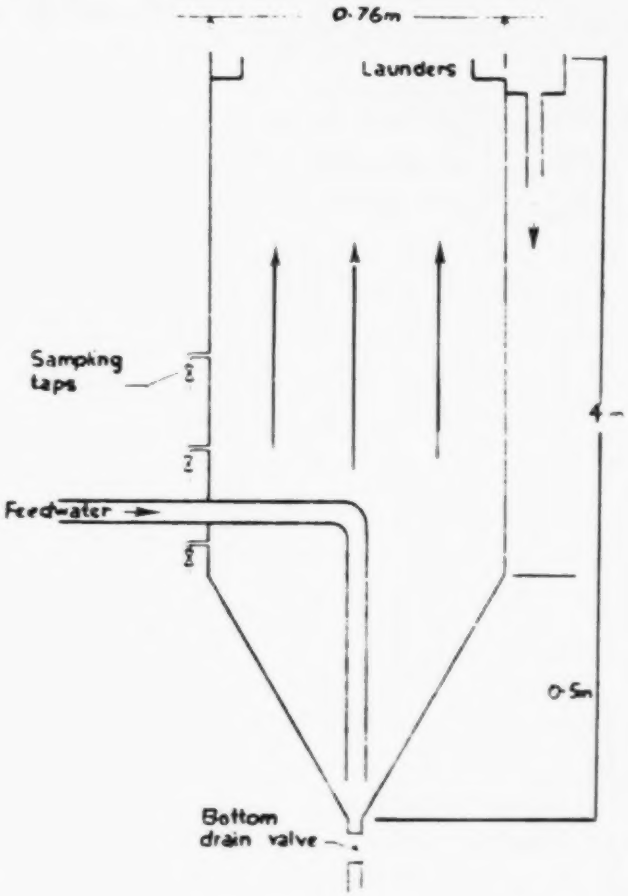


Fig. 6

Biological sedimentation tank construction

In the early experiments no seeding of the biological sedimentation tanks was carried out and even after eight months running at low upflow rates there was no floc build up in the units. Ammonia removal was poor, generally between 0 and 20%. Only when sufficient fine sand

(50-150 micron) had been added to form a detectable fluidised bed did the ammonia removal increase above 20%. Increased removal started 10 days after the addition of sand and reached a peak of 85% after 28 days. Thereafter it stabilised at around 60%.

Sixty percent removal was maintained for 35 days and then the ammonia dose was reduced from 3 mg/l to 2 mg/l. The two filters immediately began to remove 100% of the ammonia and this performance was maintained for the duration of the test.

The biological sedimentation units were evidently sensitive to raw water ammonia concentration but as the raw water contained about 10 mg/l of dissolved oxygen and theoretically this is capable of converting 2.2 mg/l of ammonia nitrogen to nitrate, the units were clearly working at full capacity - availability of oxygen being the limiting factor. (4.57 mg/O_2 is needed to convert 1 mg of ammonia nitrogen to nitrate but it was found that the loss of dissolved oxygen in the biological sedimentation units was slightly more than the theoretical figure by about 1 mg/l. It did appear, however, that oxidation of ammonia took precedence over other oxygen demands and no substance used oxygen preferentially to ammonia. A brief experiment during which pure oxygen was injected into the feed gave improved ammonia removal.)

Effect of temperature

A fall in raw water temperature from 21°C to 4°C did not affect performance although the performance of the biological filters deteriorated significantly under the same conditions and over the same period. The higher solubility of oxygen at lower temperatures is presumably a contributing factor in offsetting decreased biological activity at lower temperatures (Fig. 2).

Concentration of fluidised solids

At one stage in the work the ammonia removal efficiency dropped from 100% to 60%. This was shown to be due to a reduction in the concentration of fluidised solids. (Fluidised solids concentration was measured as the percentage solids volume after four minutes settling - very little further settlement occurs after four minutes.) Ammonia removal was found to be practically zero for fluidised solids concentrations less than 15%.

Low water temperature, which increases viscosity, will reduce fluidised solids concentration by expanding the bed further than the same flow velocity at higher temperature. This effect can be eliminated by keeping fluidised solids concentration above 35% as above this figure changes do not effect efficiency.

Conclusions

Biological sedimentation was found to be the cheapest and most effective method for removal of ammonia from river water in the concentration range 0.1 to 2 mg/l ammonia Nitrogen. Unlike biological filtration and air stripping it was not affected by declining water temperature in the range 21°C to 4°C.

Effective operation on Thames river water required a fluidised solids concentration (measured as percent volume settled after four minutes) greater than 35% and an upflow velocity not greater than 25 m/h.

In the biological sedimentation process ammonia is preferentially oxidised before all other oxygen demands but removal efficiency is limited by the dissolved oxygen content of the raw water and the process is unlikely to be able to remove much more than 2 mg/l ammonia unless oxygen is injected or the effluent from biological sedimentation is 'polished' by chlorination.

(1) SHORT, C.S.
Removal of ammonia from river water
Technical Publication TP 101, Water Research Assoc. (1973)

(2) SHORT, C.S.
Removal of ammonia from river water
2. Technical Report, TR 3, Water Research Centre (1975)

(3) NERETNIEKS, I. et al.
Removal of ammonia from wastewater by countercurrent stripping with air - an economic study
Vatten 29 (1973), 3, 269-80

(4) IONICS, Inc.
The electro-oxidation of ammonia in sewage to nitrogen
Project No. 17010 EED, Report to Water Quality Office
USEPA, July (1970)

PURIFYING ACTION OF THE GROUND IN THE TREATMENT OF DRINKING WATER

H. Kußmaul

There are good reasons for using ground water as the preferred source for drinking water supply; because of the strong purifying action of the ground it is generally hygienically unimpeachable and balanced, at least when it comes from large-scale, porous ground-water systems with intact covering strata. No mention will be made here of the difficulties in recovering the ground water from fissured rock formations.

The purifying action of the ground is due above all to the following factors. When water penetrates underground it undergoes a filtration process in which the solid particles that can adsorb the water constituents are removed. Harmful material can then be eliminated in the ground e.g. by adsorption and ion exchange on the mineral particles and on the humus substance by precipitation in the form of sparingly soluble or insoluble compounds, possibly by co-precipitation with other substances, and organic material in particular can be degraded by bacteria.

The effectiveness of the underground purification processes is presented in this report on the example of ground water enrichment with river water, in the light of experience based on years of investigations at the river filtrate waterworks on the Lower Rhine. The process for the supplementation of the ground-water reserves by river filtration is used extensively and successfully in West Germany and in some neighbouring countries. In this process the infiltration of river water into the ground is promoted by the formation of descending funnels through feed wells in the immediate vicinity of the bank (1). In the waterworks studied the feed wells were only about 50 m from the river bank (Fig. 1). Between the wells and the river are situated other observation wells, which were likewise included in the study [6/III - 6/I]. The residence times of the river filtrate underground are on average three weeks, but fluctuations between 3 and 46 days are possible, depending on the water level of the river. The mean proportion of river water in the raw water passed on for treatment is about 80%, fluctuations of 30-100% being observed depending on the water level of the river (2).

In the discussion of the behaviour of the water constituents underground a distinction should be drawn between the organic loading, since biological degradation predominates in the former case and physico-chemical processes in the latter.

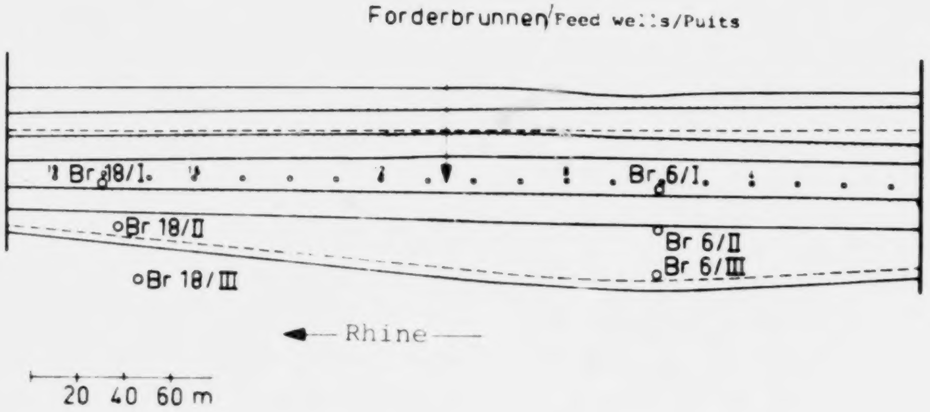


Fig. 1 Position of waterworks I on the Rhine

Organic substances

The dissolved organically bound carbon is a measure of the organic substance content of a water (DOC = dissolved organic carbon). The mean values of two waterworks are shown in Fig. 2, from which it can be seen that up to the first observation well [6/III] in the immediate vicinity of the bank of works 1 the DOC content has halved, and that no further degradation takes place during the following underground passage.

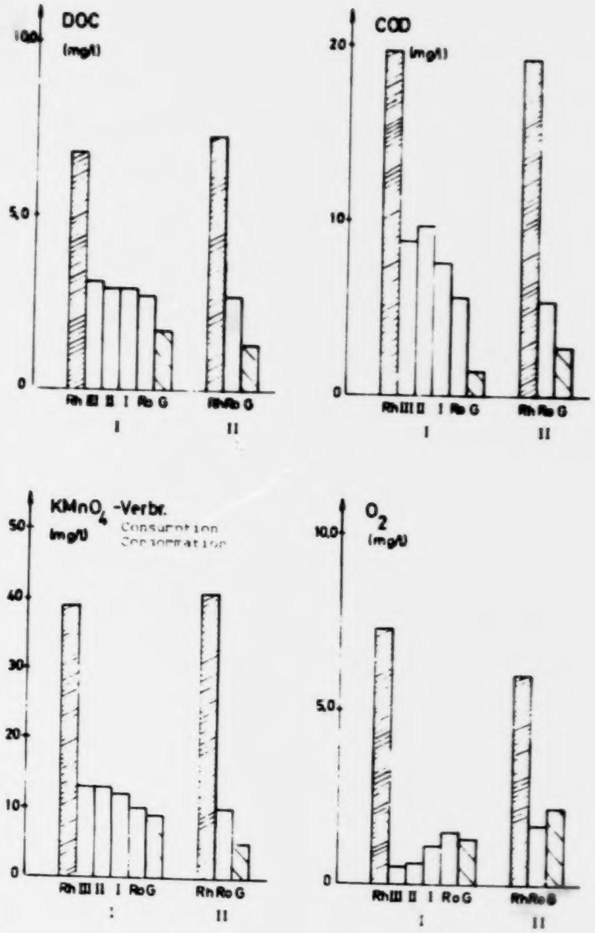


Fig. 2 Variation of the DOC, COD, $KMnO_4$ consumption, and free oxygen during underground passage (bank filtration) in two Rhine waterworks
(Rh = Rhine; III,II,I = bank filtration wells 6/III-I; Ro = raw water of the feed gallery; G = ground water)

Indications on the content of degradable organic substances in a water can be obtained from the chemical oxygen demand (COD) and the $KMnO_4$ consumption. It is found that the mean COD content of the waterworks in the immediate vicinity of the bank has also decreased by 50%, but the substances in question undergo an additional decrease during their underground passage. The $KMnO_4$ consumption falls by 68% in the immediate vicinity of the bank and undergoes no further change(Fig. 2).

The microbial degradation of organic substances is associated with a consumption of oxygen dissolved in the water. Accordingly, the lowest amount of oxygen in the water is found immediately after the loaded water has penetrated underground, and the O_2 content then rises again (Fig. 2). If the dissolved oxygen is insufficient for biological oxidation of the degradable organic substances, oxygen is released from inorganic compounds, e.g. from nitrates, which can lead to reducing anaerobic conditions in the ground water, with all their adverse effects on the nature of the water.

The elimination rates for the underground passage and the subsequent treatment of the drinking water with ozonization and active carbon filtration, calculated with an allowance for the mixing ratios of river water to ground water and the respective contents, are shown in Fig. 3. Further details of the calculations can be obtained from (3).

In Fig. 3 it can be seen that in comparison with the underground passage the drinking water treatment only reduces the DOC content further by 8%, the COD content by 20%, and the $KMnO_4$ consumption by 11%.

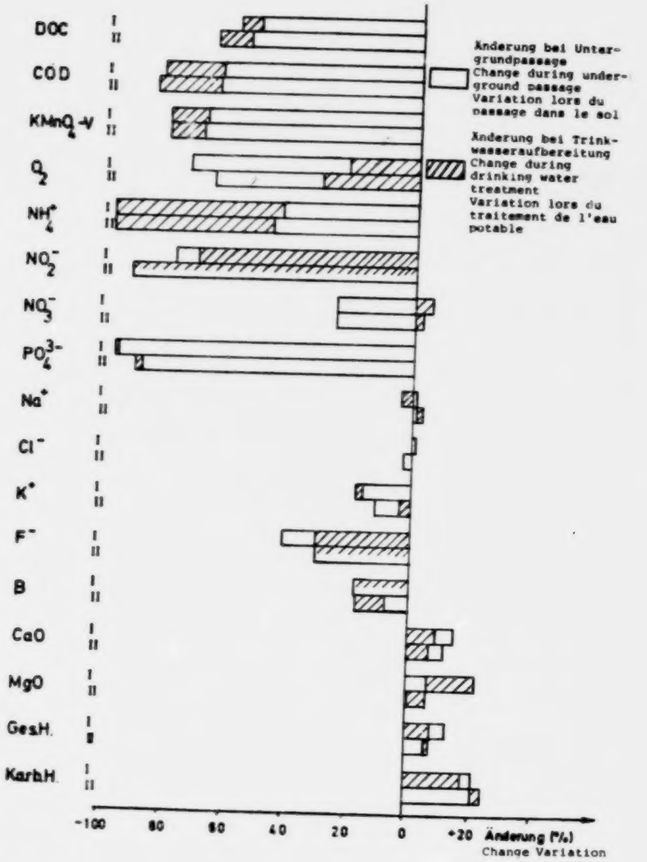


Fig. 3 Review of the concentration changes of some water constituents during bank filtration and drinking water treatment
($KMnO_4$-V = $KMnO_4$ consumption; Ges.H. = total hardness; Karb.H. = carbonate hardness)

In addition to these sum parameters for the organic loading only one other group of substances should be characterized in closer detail, this being the organochlorine compounds. Since organochlorines do not normally occur in nature, they indicate an anthropogenic origin and can therefore serve as a pollution indicator. Only about 50% of the readily volatile organochlorine compounds is eliminated during the underground passage, and after the drinking water treatment a residual content of about 20% is still present. Somewhat more favourable relationships are found for the difficultly volatile organochlorine compounds; here about 70% of the initial content is removed during the underground passage and a further 20% or so during the treatment of drinking water (Fig. 4) (4,5).

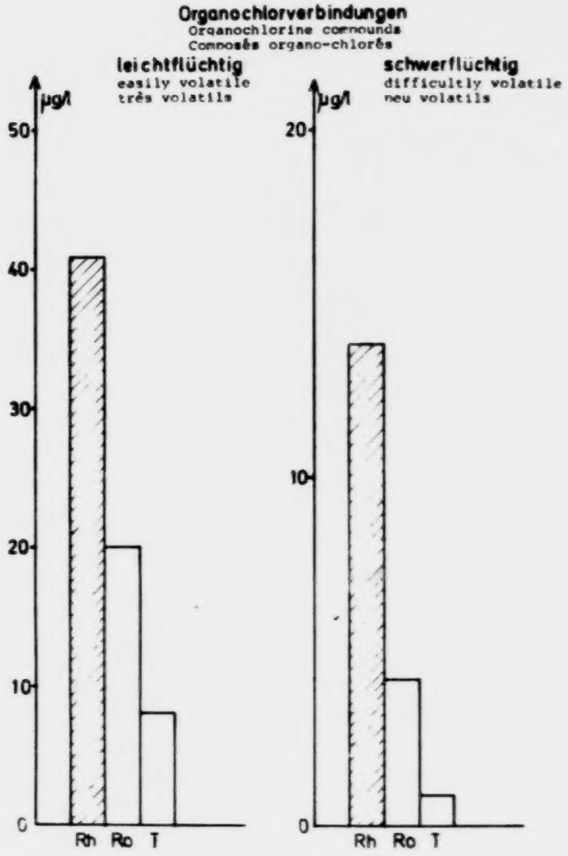


Fig. 4 Changes in the contents of easily volatile and difficultly volatile extractable organochlorine compounds during underground passage and drinking water treatment
(Rh = Rhine; Ro = raw water; T = drinking water)

The behaviour of other groups of compounds in the ground was also determined. This is described in greater detail elsewhere [6,7]. However, it was found almost invariably that the greatest purifying action took place in the immediate vicinity of the bank and that the purifying effect of the ground is very high in comparison with the subsequent treatment of the water.

However, if the individual substances are examined it is found that the retention capacity can fluctuate considerably with respect to the various components; thus, many components, even of similar composition, are retained very well, while others can pass through the ground, and often even through the drinking water treatment, suffering practically no decrease (5-7).

Inorganic materials

The concentration changes of the usual inorganic water parameters during bank filtration and drinking water treatment are described in detail in (3). Here only a summary is given (Fig. 3).

Although nitrate in the vicinity of the bank is reduced to a quarter of its original concentration, in connection with biological oxidation of the organic substances, the calculated elimination rate for the underground passage is only 26% because of the admixture of nitrate-rich ground water. After the drinking water treatment the nitrate returns approximately to the original content in the river water. This is not the case with ammonia and nitrite, which are almost completely eliminated during the underground passage and drinking water treatment. The orthophosphate content of the infiltrated river water is reduced to a residual content of a few percent in the direct vicinity of the bank. The calculated elimination rate is 95% and is only very slightly altered during the drinking water treatment.

In the case of sodium and chloride no changes take place during the underground passage and drinking water treatment. Potassium and borate show a slight decrease of 15%, and in the case of fluoride the elimination is about 33%. The hardness, given as CaO, MgO, total, and carbonate hardness, increases during the underground passage by 5-20% as the water dissolves some mineral constituents.

The elimination rates calculated for some heavy metals are shown in Fig. 5. It can be seen that zinc, chromium, and iron are retained almost quantitatively during the underground passage. Elimination rates between 50 and 71% are obtained for lead, cadmium, and mercury. Copper has an elimination rate of 11%, while an increase of 17% is established for nickel, and manganese is increased by a factor of 3. This increase in the manganese content is due to dissolution processes in the ground as a result of the weakly reducing conditions. With the exception of mercury, manganese, and nickel, no changes occur during the drinking water treatment. Manganese is almost wholly precipitated under the oxidizing conditions now present, while nickel increases by a further 85%, presumably on account of dissolution processes in the conveyor and treatment plants.

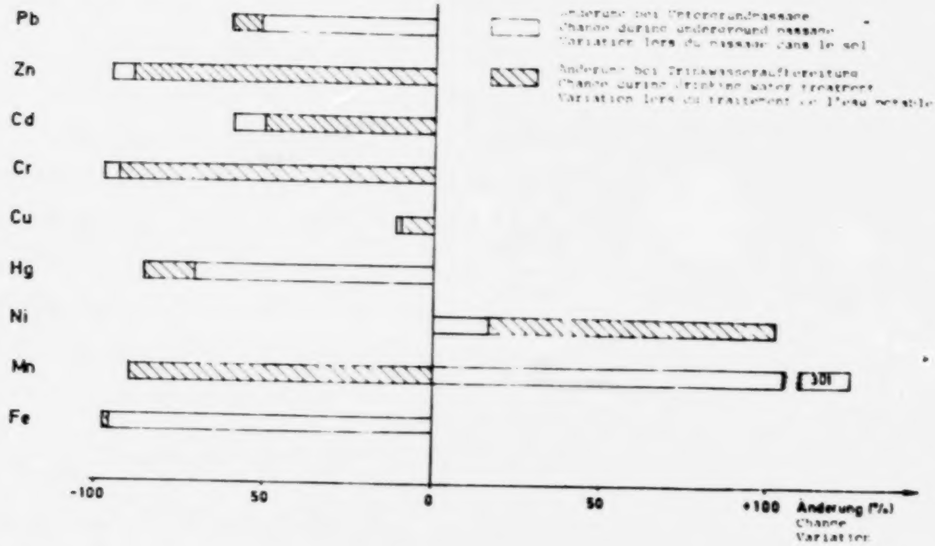


Fig. 5 Changes in heavy metal and trace metal contents during bank filtration and drinking water treatment

The numerical elimination rates given here are only valid for the conditions on the Lower Rhine. They cannot be generalized since, as can be seen in Table 1, the heavy metal concentrations in the raw water (second column) are very similar to the natural background (fifth column); they therefore correspond to the concentrations of the individual heavy metals in solution equilibria in the ground.

TABLE 1 Average 1972 and 1973 values for the dissolved shares of some heavy metals in the river water and raw water of waterworks I and II(µg/l) as well as background values

	Rhine	Raw water (= bank filtr.)	Change (%) during underground passage	"Background"
Pb	28	11	- 52	3
Zn	295	10	- 96	10
Cd	1.2	0.4	- 60	0.2
Cr	44	0.8	- 98	1
Cu	21	16	- 11	7
Hg	0.8	0.2	- 71	0.1
Ni	11	11	+ 17	3
Mn	164	534	+301	7
Fe	1132	35	- 96	50

Summarizing, as regards the removal of heavy metals, it can be stated that the elimination action of the ground under aerobic conditions is so high that only those concentrations are still present in the river filtrate that correspond to the natural background values; the retention capacity increases numerically with increasing loading of the surface water with heavy metals.

The elimination of heavy metals is, however, partly reversible. If a change takes place in the redox potential in the ground, or if larger amounts of chelate formers are present, there is a danger that the heavy metals will redissolve. This danger is increased by the fact that considerable amounts of heavy metals are bound in the sediments and the suspended matter of the river, and these can also pass into solution under anaerobic conditions. This is especially dangerous for river filtrate waterworks, since the current water-treatment processes are not particularly suited to the removal of heavy metals.

Summary

The results of the investigations indicate that the inorganic and organic loading of river water is reduced immediately after penetration into the ground by filtration, adsorption, precipitation, or microbial degradation. However, some of the material is not retained during the underground passage or the drinking water treatment. The man-made foreign substances are particularly important in the evaluation of the safety of drinking water supplies.

The penetration of highly charged river water underground during ground water enrichment by bank filtration is admittedly an extreme case. However, taking into account the low loading of harmful materials in precipitation water, the present results also allow conclusions to be drawn on the possible endangering of ground water in natural groundwater formation.

(1) BMI-Fachausschuß "Wasserversorgung und Uferfiltrat"
Uferfiltration, Bonn 1975

(2) KUSSMAUL, H., MÜHLHAUSEN, D., BEHRENS, H.
Hydrol. und hydrochem. Untersuchungen zur Uferfiltration
Teil I: Chlorid, Borat und Uranin im Flußwasser als Leitsubstanzen zur Ermittlung von Verweilzeiten und Mischungsverhältnissen bei der Trinkwassergewinnung durch Uferfiltration
gwf-Wasser/Abwasser 118 (1977), 521-524

(3) KUSSMAUL, H., MÜHLHAUSEN, D.
Verweilzeiten, Mischungsverhältnisse und Veränderungen der Wasserbeschaffenheit bei der Uferfiltration am Niederrhein
WaBoLu-Bericht 42 (1977)

(4) KUSSMAUL, H.
Behaviour of Persistent Organic Compounds in Bank-filtrated Rhine Water
Aquatic Pollutants - Transformation and Biological Effects, London (1978), 265-274

(5) KUSSMAUL, H., FRITSCHI, U., FRITSCHI, G., SCHINZ, V.
Leichtflüchtige Halogenkohlenwasserstoffe im Rheinwasser, Uferfiltrat und Trinkwasser
WaBoLu-Bericht 3 (1978), 75-85

(6) HEGAZI, M.
Analytik und Verhalten von Phenylharnstoff-Herbiziden und deren Metaboliten bei Uferfiltration, Trinkwasseraufbereitung und Bodenpassage
Diss. Bonn 1977

(7) FRITSCHI, G., KUSSMAUL, H., SONNENBURG, J.
Cholinesterase-hemmende Stoffe im Oberflächenwasser, Uferfiltrat und Trinkwasser
WaBoLu-Bericht 40 (1976)

BEHAVIOUR OF MICROPOLLUTANTS IN RIVER WATER DURING BANK FILTRATION

G.J. Piet and C.F. Morra

1. Abstract

The analysis of individual organic chemicals in water of the river Rhine and of this water after bankfiltration gives an idea of the behaviour of organic compounds during passage through the soil.
Chemicals which pass into the drinking water supply are selected, their maximum concentrations are listed and a notation is made when they belong to a suspected group of chemicals. Means are indicated to prevent drinking water pollution by industrial compounds. Recommendations are given for future research on substances which impair the quality of drinking water derived from bankfiltered riverwater.

2. Introduction

Bankfiltered water can become important for the drinking water supply in The Netherlands. In the year 1976 drinking water was abstracted from groundwater (700 mill.m^3) and from surface water (400 mill.m^3) with the expected increase of drinking water consumption more and more surface water has to be used because of the limited availability of local groundwater (1). In The Netherlands a use of 250 million m^3 bankfiltrated water for the drinking water supply is foreseen which quantity could be extended to 1000 million m^3/year after the introduction of revised structural plans. The advantages of bankfiltration such as a reduction in the concentration of organic pollutants disinfection without the application of chemical oxidation, reduced influence of calamities in the river on the quality of the bankfiltered water when residence times in the soil are sufficiently long, the fact that the water is stored in a protected place where organisms which can introduce unwanted metabolites cannot affect the water quality, make it a good and non-expensive water treatment system.

The information on bankfiltration is also of importance to other infiltration techniques such as dune infiltration and groundwater recharge in combination with slow sandfiltration. A close examination of the processes which take place in the soil is of great value to select additional techniques such as activated carbon treatment necessary to produce wholesome and agreeable drinking water when heavily polluted river water is used as raw water source (2, 3).

The quality of drinking water derived from bankfiltered Rhine water is affected by organic compounds, particularly industrial chemicals which pass into the drinking water supply.

Suspected chemicals or groups of chemicals have to be considered in relation to the long-term effect on human health and to the odour and taste of finished water. It is important to have knowledge of the processes which play a role in the reduction of organic chemicals during passage in the soil. Chemicals which endanger the quality of drinking water from bankfiltered Rhine water have to be selected.

3. Organic chemicals in water of the river Rhine which affect the drinking water quality

In tapwater from bankfiltered sources more than 200 organic substances have been identified and subsequently quantitatively measured by analytical procedures based on a gas-stripping technique and a XAD adsorption technique (4). The analysis of Rhine water is carried out by an extraction technique with cyclohexane-diethylether and by means of a static head-space method (5, 6). A capillary GC-MS system is used for identification. Special attention is given to those chemicals which are present in river water and pass during bankfiltration. A thorough chemical analysis of tapwater from three water production plants using bankfiltered Rhine water was made to select suspected chemicals.

The selection of compounds was made on the basis of the following criteria

- Experimental evidence of toxicity for man or animals including carcinogenity, mutagenicity and teratogenicity (7)
- Identified in drinking water at relatively high concentrations
- Molecular structure closely related to other toxic or odour-intensive compounds
- A known odour threshold concentration in water which is 1% or less of the actual concentration (8).

In the investigated water plants only aeration and rapid sand filtration is applied after bankfiltration. The time of residence in the soil is at least 100 days in all cases.

4. Organic chemicals in drinking water from bankfiltered Rhine water after passage of the soil

The selected organic chemicals analysed in finished water from bankfiltered Rhine water in The Netherlands are listed in Table I. Though the concentrations of these substances differ from place to place due to different conditions of the soil passage, usually the same type of compounds appears at different plants.

Table I

Selected organic chemicals in tapwater from bankfiltered Rhine water in The Netherlands
(maximum concentration in ng/litre)

Component	Max. conc. ng/litre	
chloro-ethers		
bis(2-chloroethyl)ether	30	suspected animal carcinogen
bis(2-chloroisopropyl) ether	3000	
chloro-benzenes		
chloro-benzene	30	
o-dichloro benzene	100)	
m-dichloro benzene	100)	
p-dichloro benzene	300)	
ε-trichloro benzenes	300	
chloro-methyl benzene	5	
chloro-alkanes and alkenes		
chloroform	300	suspected animal carcinogen
tetrachloromethane	100	suspected animal carcinogen
1,2-dichlorethane	500	
tetrachlorethene	50	
1,2-dichlorpropane	300	
trichlorethene	500	
other chloro compounds		
chloro aniline (m,p)	1000	
5-chloro-o-toluidine	300	
tri(2-chloroethyl) phosphate	100	

(continued)

component	Max. conc. ng/litre
aromatic chemicals	
benzene	present
toluene	100
ethylbenzene	30
o-xylene	30
m/p-xylene	100
c_3-benzenes	1000
c_4-benzenes	100
others	
naphtalene	100
divinylbenzene	30
2-methylnaphtalene	30
acenaphtene	30
biphenyl	100
anthracene	30
pyrene	30
alkanols, aldehydes	
c_5-alkanols	300
c_9-alkanols	100
geosmin	10
dimethylbenzaldehyde	1000
cinnamaldehyde	300
others	
oxygen-containing components	
1,1-dimethoxy propane	100
1,1-dimethoxy isobutane	300
bis(3-methoxy-ethyl)ether	300
bis(2-methoxy-2-ethoxy)ether	100
methylisobutyrate	100
dimethyl acetophenon	100

(continued)

component	Max. conc. ng/litre
triethyl phosphate	1000
tributyl phosphate	30
3 unknown compounds	300 - 1000

It is evident that several industrial chemicals are not fully eliminated even during long residence times in the soil.
Some lower esters and ethers, which improve the odour quality of water are present after groundpassage.
It is not fully understood whether bis(2-chloroethyl)-ether is formed during groundpassage or not.
Some aromates have rather low odour threshold concentrations (such as naphthalene, mesitylene etc.). Toluene, xylenes, and ethylbenzene are substances which may affect water quality too.
Polynuclear aromatic hydrocarbons are mainly presented by fluoranthene and always in concentrations below 50 ng/litre.
The concentration of alkanes, with exception of C_{10}-alkanes was always below the 100 ng/litre level.
An important reduction of several chemicals can be reached if the residence times are sufficiently long.
For this reason a consideration of the analysis of the river water of the Rhine is of interest.

5. Organic chemicals in the river Rhine

The investigation of the water of the river Rhine is performed by the same instrumental analysis as the bank-filtered water, and it became evident that the following major compounds in the Rhine water are almost completely removed during groundpassage (Table II).

Table II

Organic chemicals at concentrations > 1 µg/litre in Rhine water which were not detected in related tapwater (9)

Component	Concentration (µg/litre)
nitrobenzene	1 - 10
o-nitrotoluene	10
m-nitrotoluene	1
p-nitrotoluene	3
di-nitrotoluene	1
p-nitro aniline	1
N-ethyl aniline	1
N.N.-diethyl aniline	1
amino-nitro toluene	3
diphenyl amine	1
m/p-chloro nitro benzene	1
o-chloro nitro benzene	1
m/p-chloro toluene	1
o-chloro toluene	1
methyl-tert.butylphenol	1
diethylene glycol diethylether	1
2,6-di(t)butyl-1,4-benzoquinone	2
2(methyl-thio)benzo thiazol	1

It is of interest that some of these chemicals seem to be rather persistent to microbial decomposition in river water, they are eliminated, however, during passage of the soil.

The chlorinated butadienes, chlorinated phenols and cresols are not found as major contaminants in The Netherlands. The same is true for o-phenyl-phenol, p-nitro-phenol, phenol, m-cresol and 2,4-dimethyl phenol (10).

Though a great diversity of industrial pollutants is present in Rhine water, only a limited number passes into the drinking water in The Netherlands at concentrations > 10 ng/litre.
Several processes involving the reduction of organic chemicals during bankfiltration are similar to those during slow sand filtration where mainly microbial decomposition modifies organic compounds. In 2 water treatment plants using slow sand filtration techniques after dune infiltration of river water, the following compounds were present in concentrations > 10 ng/litre (see Table III).

TABLE III Organic chemicals in drinking water after dune infiltration and slow sand filtration of polluted river water (concentrations > 10 ng/litre)

alkanes	: C_8-C_{11} alkanes
alkyl benzenes	: toluene, C_3-benzenes, C_4-benzenes, ethyl styrenes
naphthalenes	: naphthalene
alkanols	: C_5-C_7 alkanols
aldehydes	: dimethyl benzaldehyde, cinnamaldehyde
ketones	: acetophenone
ethers	: 1,1-dimethoxy isobutane
esters	: ethyl acetate, butyl acetate
phtalates	: dimethyl-, diethyl-, dibutylphthalate
organo-halogens	: tetrachloromethane, trichloroethene, tetrachloroethene,hexachlorobutadiene, chloro benzene, o-dichlorobenzene, p-dichloro-benzene, bis-(2-chloroisopropyl)ether
nitrogen-containing compounds	: N-ethyl aniline
sulfur-containing compounds	: benzo thiazole

A correlation between some chemicals which are not completely removed by slow-sand filtration and bank filtration is evident.

6. Processes which play a role during bankfiltration

Filtration of particulate matter with adsorbed organic chemicals such as PAH's, PCB's, pesticides and insecticides, high-boiling hydrocarbons leads to the reduction of the concentration of several organic contaminants during passage of the soil. Adsorption and ion exchange will also take place.
In the case of precipitation of e.g.carbonates and sulfides co-precipitation of organics can occur. This is, however, a slow process where the equilibrium between dissolved and precipitated substances is time-dependent (11). Chemical reaction such as hydrolysis can occur also.

Microbial decomposition,under aerobic and an-aerobic conditions, the presence or nitrates for the additional supply of oxygen affect for a great deal the decomposition effect of organic chemicals in the soil. The degradability of compounds which decreases with the increasing number of halogen atoms and depending on the type of halogen atoms oftentimes determins the fate of organics in the soil (11). Several organo-chlorine compounds which are not readily adsorbed seem to survive. For this reason after-treatment of bankfiltered water should be performed with strong adsorption procedures such as activated carbon treatment. But even when this procedure is applied after ozonation of bankfiltered water substances such as chloroaniline, chloroform, dichlorobenzene, tetrachloromethane,1,2-dichloroethane,dibutylphthalate,C_3 benzenes, C_{10} alkanes, triethylphosphate and some unidentified substances were not completely removed during the processes in a drinking water plant. Water sanitation programs have to be installed to improve drinking water quality while structural plans to

increase residence time in the ground are also necessary. Recharge of groundwater leading to a certain dilution of pollutants is of assistance to provide a good quality drinking water from polluted surface water.
Pretreatment processes, such as flocculation which removes organic material but more so ozonation which improves the biodegradability of organic substances and makes these better adsorbable, are recommended to improve the quality of bankfiltered water.
In the case of possible mobilization of chemicals or a certain degree of "saturation" of the ground after prolonged use of bankfiltration, model studies as will be performed at the National Institite for Water Supply (11) are of assistance. The fate of chemicals during passage of the soil can be better predicted when more insight into the processes taking place in the soil is obtained.

7. Conclusions and recommendations

- Bankfiltration is a safe, inexpensive and reliable technique of water treatment
- Suspected chemicals which "break through" have to be monitored and proposed for surface water sanitation programs
- Structural plans have to be developed to attain optimal residence in the ground if possible
- Some fundamental studies of mobilization of chemicals have to be set up
- Additional treatment systems, necessary to produce a wholesome and agreeable type of drinking water are necessary when bankfiltered Rhine water is used for the drinking water supply
- The introduction of pre-treatment of bankfiltered water by flocculation and/or ozonation can be of great importance.

(1) ZOETEMAN, B.C.J.
Kwalitatieve beschikbaarheid van grond- en oppervlaktewater
H_2O 8 (1975), 4, 75-81

(2) SONTHEIMER H., NISSING, W.
Änderung der Wasserbeschaffenheit bei der Bodenpassage unter besonderer Berücksichtigung der Uferfiltration am Niederrhein
Gas-Wasser-Abwasser 57 (1977), 9, 639-645

(3) ROBERTS, P.V. et al.
Groundwater recharge by injections of reclaimed water in Palo Alto
Civil Engineering Technical Report No. 225, Dept. of Civil Eng., Stanford University, Stanford, Ca. (1978)

(4) ZOETEMAN, B.C.J.
Sensory assessment and chemical composition of drinking water
Thesis, National Inst. for Water Supply, Leidschendam, The Netherlands

(5) PIET, G.J. et al.
A fast quantitative analysis of a wide variety of halogenated compounds in surface- drinking- and groundwater
Internat. Symp. on the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, Hamilton, Ontario, Canada, May 23-25 (1978)

(6) PIET, G.J. et al.
Determination of very volatile organic compounds in water by means of direct head space analysis
Analytical Letters, A11 (1978), 5, 437-448

(7) Drinking Water and Health
At the request of and funded by the U.S. Environmental Protection Agency, National Academy of Sciences, Washington, D.C. (1977)

(8) Van GEMERT, L.J., NETTENBREIJER, A.H.
Compilation of odour threshold values in air and water
National Inst. for Water Supply; Central Inst. for Nutrition and Food Research, TNO, Zeist, The Netherlands (1977)

(9) MORRA, C.F.
Internal communic., National Inst. for Water Supply, The Netherlands (1978)

(10) SMIT, Z.
Determination of some phenolic compounds by concentration on XAD resins and T.L.C.
Internal communication, National Inst. for Water Supply, The Netherlands (1978)

(11) HARMSEN, K.
Column and adsorption experiments to be performed for the examination of the quality of groundwater in The Netherlands (in Dutch)
Internal communication, National Institute for Water Supply, The Netherlands (1978)

EXPERIENCE WITH THE REMOVAL OF MICROIMPURITIES IN SLOW SAND FILTERS

K. Schmidt

The behaviour of an impurity in water and the degree of its elimination in a biologically active filter are determined primarily by the following factors:

1. Chemical and physical properties of the impurity material.
2. Concentration, loading duration, and origin of the impurity.
3. Biological assimilability or persistence of the material.
4. Concentration and nature of the animate and inanimate organic charge of the filter material.
5. Possible reactions of the unwanted substance with other substances present in the system.
6. Functions of the active agent of the unwanted substance.

A number of other material properties and mechanisms relevant to elimination could be added to this list, but these are mostly of secondary importance.

As regards its construction and the reactions taking place in it, a slow sand filter has a very complicated structure, and the individual factors are connected to one another by numerous interrelationships and regulation circuits. It is therefore difficult to trace the exact course of the elimination of an unwanted substance in detail and to interpret it satisfactorily from the scientific point of view. The empirically established performance of a system is difficult to fit into known patterns and its applicability to other times or to other places is limited to at least an order of magnitude.

The principal factors in the elimination of impurities from water, given in the preceding list, will now be considered in closer detail.

1. Chemical and physical properties of the impurity material

The chemical and physical material properties that have a bearing on elimination in biological filters are as follows:

1. Hydrolysability.
2. Solubility in water.
3. Polarity.
4. Volatility.
5. Molecular structure.
6. Molecular size.
7. Electrical charge.

It is generally known that polarity, solubility in water and molecular size are factors decisive for the adsorbability of a given compound. The molecular structure determines the compound's degradability, and the electrical charge and the charge distribution determine the behaviour with respect to other dissolved and undissolved constituents. Different materials vary strongly in these properties, giving rise to correspondingly different patterns of behaviour.

2. Concentration, loading duration, and origin of the impurity

The significance of the loading duration and concentration for the elimination of an unwanted substance in biological filters is presented in Table 1. Normally the unwanted materials are present in surface waters as a permanent more or less uniform loading and usually in low concentrations. If the substances are degradable, they are removed efficiently by the biological action of a slow sand filter. However, many persistent substances break through, usually after a shorter or longer delay. In the long run only that fraction is removed which is removed from the system with the topmost sand layer when the filter is cleaned.

TABLE 1 Significance of the duration and concentration in loading with undesirable substances for their elimination in biological filters

Type of loading	Material properties	Behaviour in the filter
Continuous loading Relatively low concentration (e.g. waste water pipes)	readily degradable	good elimination
	difficultly degradable	good elimination
	persistent,adsorbable	restricted elimination
	persistent, non-adsorbable	no elimination
Sudden loading Relatively high concentration (e.g. transport accident)	readily degradable	anaerobiosis
	difficultly degradable	inital break-through
	persistent,adsorbable	good elimination
	persistent, non-adsorbable	no elimination

In the case of sudden loadings, e.g. after accidents, the unwanted materials are present for only a short time but usually in relatively high concentrations. Readily degradable substances cause an intensified oxygen consumption, which can give rise to anaerobic conditions in the system. Sudden and heavy loadings with impurities that can only be degraded after an adaptation pass through the filter in so far as they are not very readily adsorbable.

Short-term increases in the concentration of persistent adsorbable substances are well intercepted and often pass through the filter with a long time delay, the concentrations being frequently reduced by two to three powers of ten.

Table 2 shows the behaviour of biogenic impurities in biological filters. Many organic substances are formed by the microorganisms in the water and in the slow sand filters. Even in main canals loaded with sewage more than half of the organic carbon can be of biogenic origin. It is known that many of the substances responsible for undesirable taste and smell of the water are released by algae and actinomycetes. Some excreta are highly stable as metabolic end products in the given system. They can also pass through biologically active filters and cause serious problems in the production of drinking water.

3. Biological assimilability or persistence of the material

Various types of biological degradation in filters are shown in Table 3. Most organic materials are bio-degradable. If they can be assimilated by many bacterial species, their elimination will be spontaneous and far-reaching. Sometimes a necessary adjustment of the intracellular metabolism is responsible for a certain delay in the degradation (enzymatic adaptation). A longer "running-in" time is needed if the substance concerned can only be utilized by a small number of specialized organisms whose proliferation is initiated by the impurity substance itself.

TABLE 2 Behaviour of biogenic impurities in biological filters

Origin	Material properties	Behaviour in the filter
Normal plankton content	readily degradable	good elimination
	difficultly degradable	good elimination
	persistent, adsorbable metabolic end-products	restricted elimination
	persistent, non-adsorbable metabolic end-products	no elimination
Destruction of a mass population	readily degradable	anaerobiosis
	difficultly degradable	initial break-through
	persistent, adsorbable metabolic end-products	good elimination
	persistent, non-adsorbable metabolic end-products	no elimination

TABLE 3 Various types of biological degradation in filters

Spontaneous degradation without adaptation by several species
Slightly delayed degradation after enzymatic adaptation
Delayed degradation, only by "specialist" bacteria
Slow degradation as a secondary metabolic reaction
Final degradation to inorganic end-products
Incomplete degradation only as far as organic "refractory" end-products
No degradation of persistent organic materials

Many harmful substances can only be transformed in secondary metabolic processes, the microorganisms involved then requiring other organic materials for their basic nutrition. Their proliferation therefore cannot be controlled by the harmful substance.

Not all degradable substances can be mineralized in biological filters to inorganic end-products. Under certain conditions biologically stable metabolic products are formed, which can only again become assimilable after far-reaching changes in the medium (e.g. a shift of the redox potential).

4. Concentration and nature of the animate and inanimate organic charge of the filter material

Both the biological degradation and the adsorption processes take place predominantly in the top few centimetres of the filter bed, in which layer the suspended detritus is fixed and the autochthonous filter fauna and flora develop most intensively. Both are absent in new filters and must be established in the course of a fairly long running-in time. In filters exposed to the light algae play an essential part in the elimination of undesirable materials.

Fig. 1 shows schematically the phases involved in the substance conversion on the example of the degradation of a readily soluble compound: the granular skeleton of the filter material, the accumulated clay minerals, the biological population of the filter material consisting of algae, bacteria, and fungi, the embedded suspension material, some of which consists of particulate organic carbon, the water phase, and the harmful material degraded by bacteria with the aid of nutrients, a harmless degradation product being formed in this case. The arrows indicate the intensity of the material transport. It should be emphasized that biological filters are self-regulating in response to

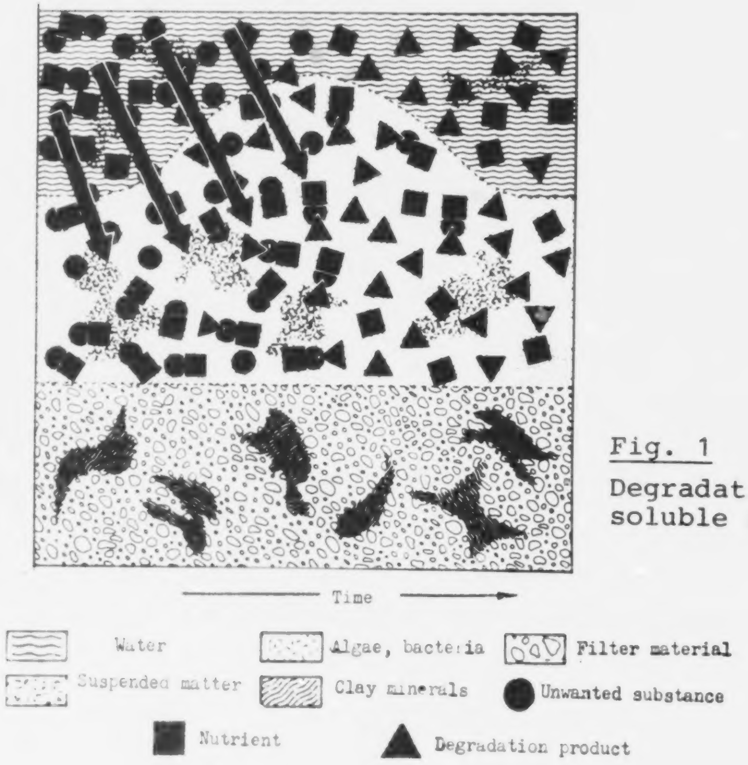


Fig. 1

Degradation of a readily soluble substance increases in the concentration of degradable materials in the raw water: the microorganisms which perform the degradation proliferate and thus provide additional adsorption sites and increased degradation capacity.

Fig. 2 shows the material transport for the case of a sudden loading with a non-degradable, readily adsorbable substance. This is fixed mainly on the organic material in the topmost layer of the filter bed. A small proportion not fixed here can also be fixed deeper in.

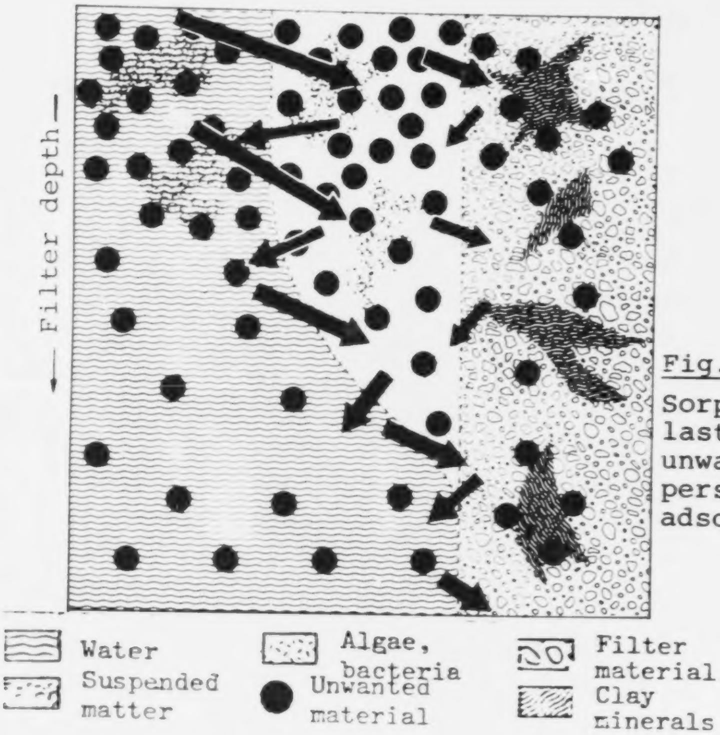


Fig. 2

Sorption after short-lasting loading of unwanted material: persistent, well-adsorbable

If the loading with persistent harmful materials continues for a longer time, the conditions in the upper layers approach a state of equilibrium with a corresponding concentration of the material (Fig. 3). The region of particularly intensive fixation of harmful material is gradually displaced in the direction of greater depth. When layers with little or no biological growth have been reached, for many materials the adsorption capacity of the solid phase decreases and the passage through the filter bed is considerably accelerated.

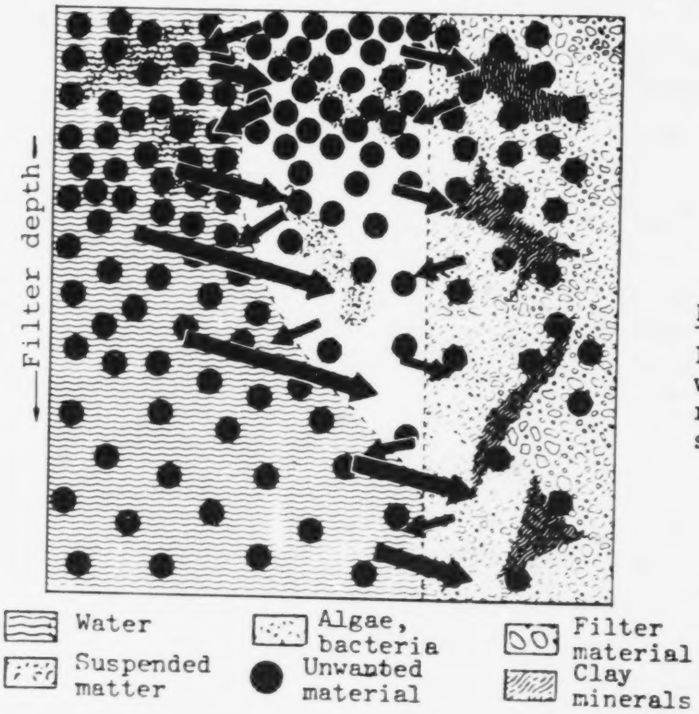


Fig. 3

Long-lasting loading with a persistent, readily adsorbable substance

If the contamination of the raw water decreases the material equilibrium between the water and the solid phase is perturbed and the material is desorbed until a new equilibrium has become established (Fig. 4). Desorption processes in the case of fluctuating water quality sometimes result in higher concentrations of unwanted materials at the filter outlet than in the raw water itself.

If the biological growth suddenly dies off and decomposes, the adsorbed or accumulated harmful substances are once more released (Fig. 5). This can happen when, e.g. iron bacteria die as a result of an oxygen deficiency. The best example, however, is the release of harmful materials from decomposing algae, with high enrichment factors for many substances.

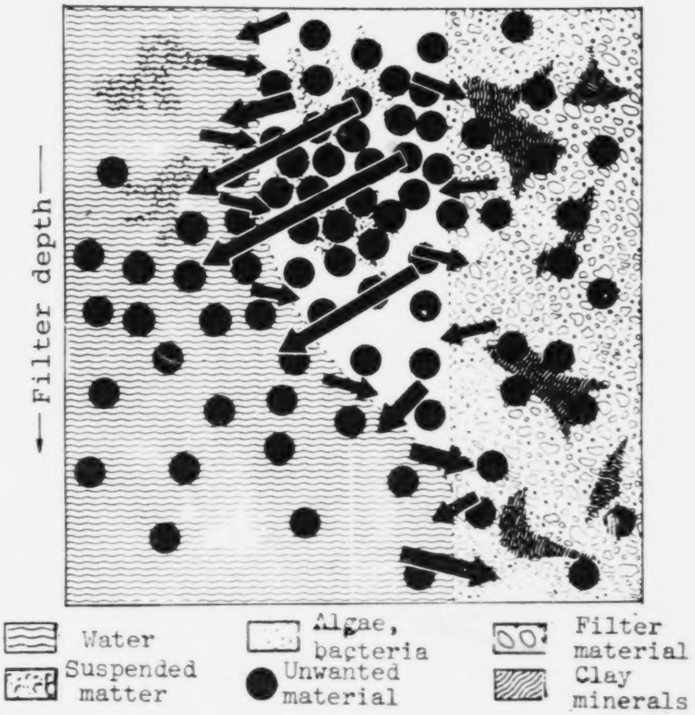


Fig. 4

Desorption after temporary loading with a persistent, well adsorbable material

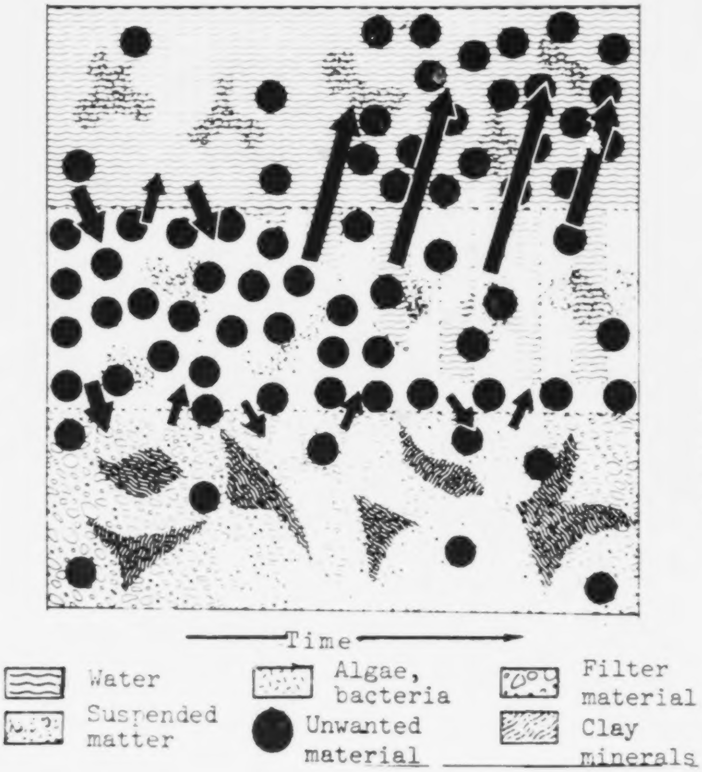


Fig. 5

Release of unwanted materials on destruction of the biological growth due to a change in the medium

The topmost zone of the filter,which is particularly biologically active, plays a major part in all these reactions.

5. Possible reactions of the unwanted substance, with other substances present in the system

By reacting with other water constituents an unwanted substance can be removed from adsorption equilibria primarily set up and be fixed more or less finally. Examples of this are the sulphide precipitates of some heavy metals under anaerobic conditions and the precipitation of manganese as manganese dioxide or of iron as the hydroxide.

Another manner in which a substance can be removed from an equilibrium between the liquid and the solid phase is by complexing with natural or anthropogenic complex formers.

The active accumulation of harmful substances within the cells of microorganisms can also be viewed in this way.

6. Functions of the active agent

Many constituents of water exert an inhibitory or promoting action on reactions of other substances. Phosphate promotes the proliferation of bacteria without increasing the loading of the organic matter (1). The degradation of higher hydrocarbon loadings can be accelerated by the addition of bound nitrogen (2). The addition of growth substances, e.g. vitamins, can also enhance the degradation. Many substances stimulate bacterial activity at low concentrations and inhibit it when their loading is higher.

As a biological system, a slow sand filter is highly susceptible to certain influencing factors, yet on the other hand it can be very adaptable. The physical filtration processes taking place within it provide an additional security. Thus, in the case of a sudden loading with a bacterial substance, its concentration can be reduced to such an extent in the upper filtration layer that the lower-lying regions of the filter can still fulfil their degradaction function. This is the case, for example, in the addition of chlorine to combat algae.

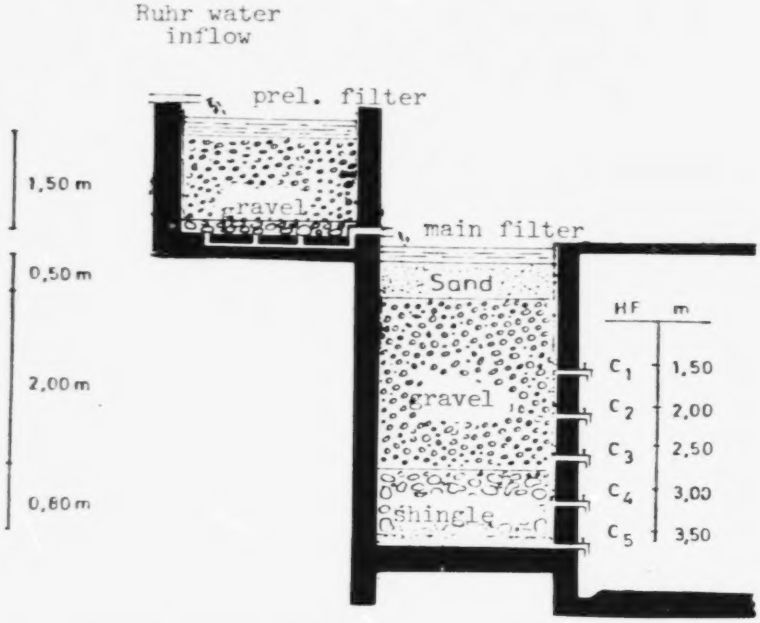


Fig. 6 Preliminary filter - main filter system (experimental ground-water plant)

It is not feasible to illustrate systematically all the above-mentioned processes by quoting relevant experimental results. The publications of the Dortmund Water Research Institute over the last 15 years should be consulted for this purpose. Some examples, most of which were obtained in the experimental plant shown in Fig. 6, can, however, be given to clarify the above statements.

In Fig. 7 it can be seen how after a trial with additions of cadmium strongly increased cadmium concentrations were produced in the wash-out phase by sudden destruction of the algal population right up to deep regions of the filter bed (3). This demonstrates the high rate of fixation in algae during the introduction of cadmium and remobilization of the fixed cadmium when the algae die off, as well as the release of complex formers from the algal material, which prevent renewed fixation of the cadmium in subsequent passage through the filter.

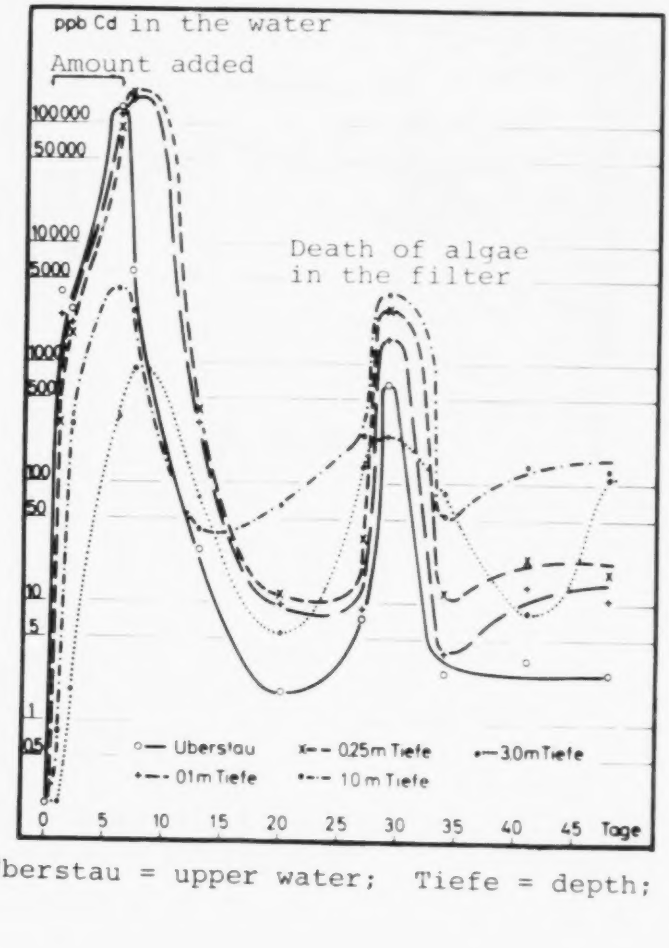


Fig. 7

Remobilization of cadmium on death of an algal population

Überstau = upper water; Tiefe = depth; Tage = days

The preferred fixation of microimpurities in the organic material of the upper filter layers is demonstrated in Figs. 8 and 9.

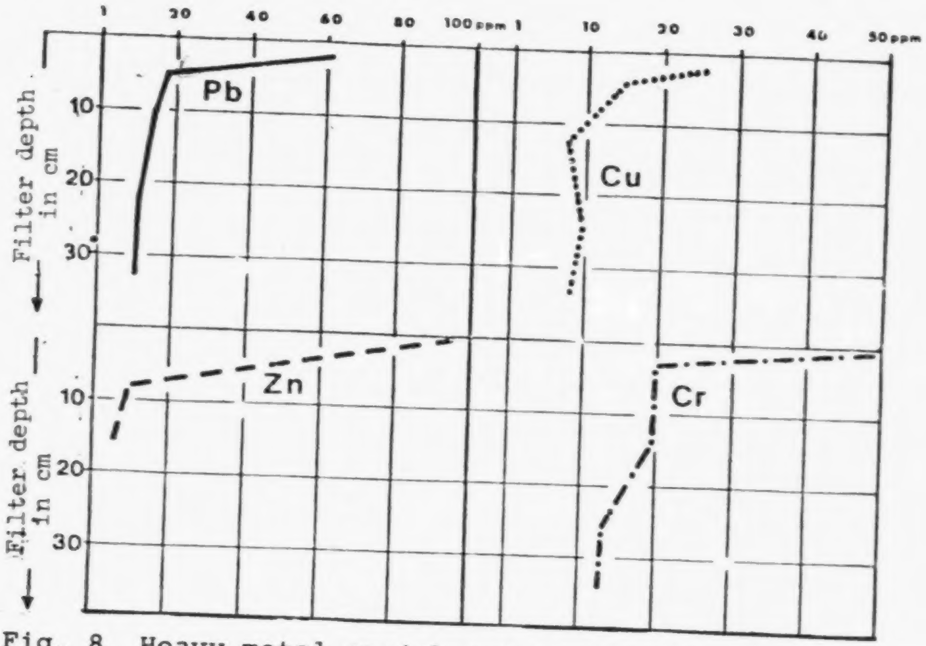


Fig. 8 Heavy metal enrichment in the filter sand in long-term addition experiments

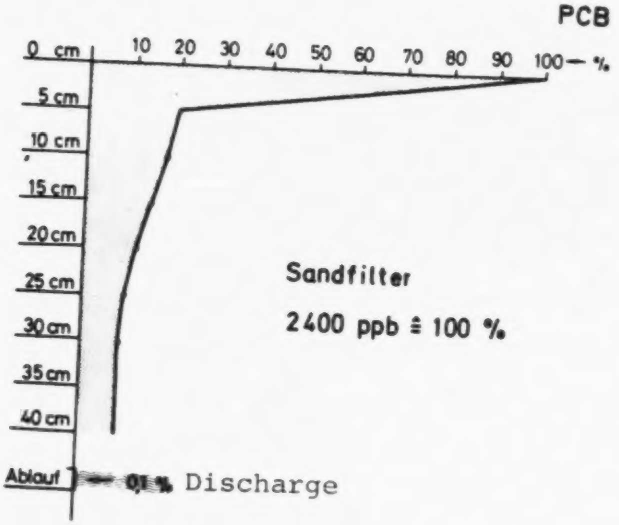


Fig. 9 Percentage decrease of CLOPHEN A 30 against filter depth at the end of the trial; experimental groundwater plant

Fig. 8 shows the enrichment of lead, copper, zinc, and chromium in the upper sand layers after heavy metals have been introduced over a period of several months (4).

Fig. 9 illustrates the PCB content of the filter sand in a dosage trial after a three-year wash-out phase (5). Even after this long time the greater part of the fixed PCB is still present in the top few centimetres of the filter bed. It is also clear that when the slow sand filters are cleaned a considerable fraction of the harmful substances introduced is removed from the system.

The illustrated adsorption processes can also delay the break-through and even out the sudden loadings occurring in the raw water to a considerable extent, even over relatively short sections of the filter bed. Fig. 10 represents, on the example of hexachlorobenzene, a break-through delayed by 4 weeks with a reduction of the concentration by two powers of ten (6).

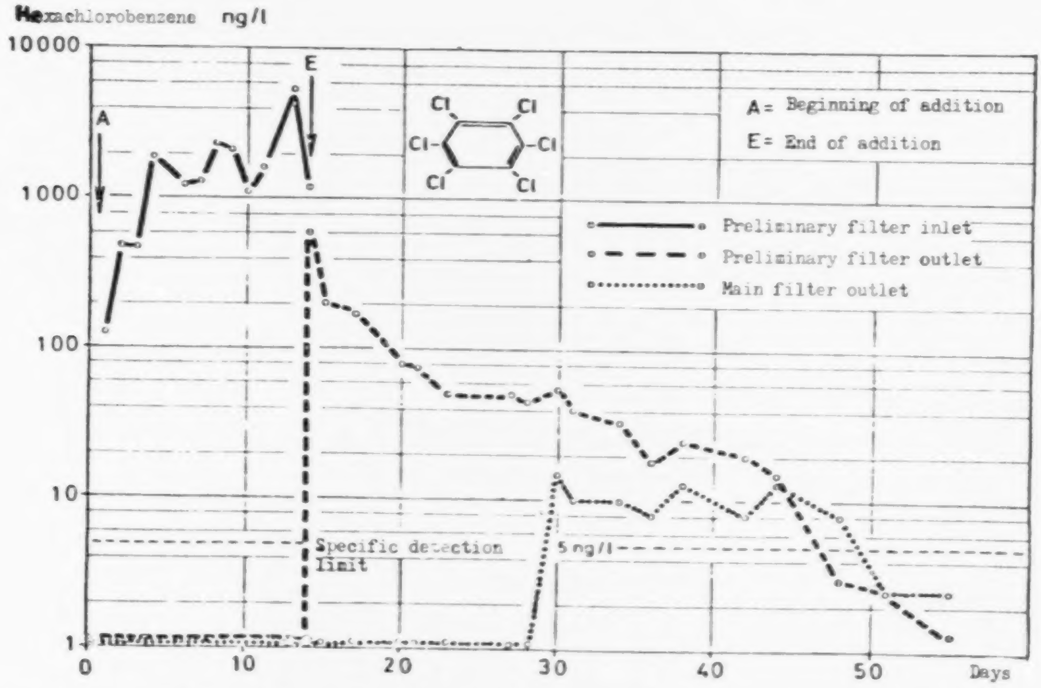


Fig. 10 Delayed breakthrough of hexachlorobenzene in a preliminary filter/main filter system

Fig. 11 shows the course of the concentration as a function of time, at various depths in the filter, after a sudden copper addition (4). It is clear that the concentration decreases with increasing depth and the loading duration becomes longer.

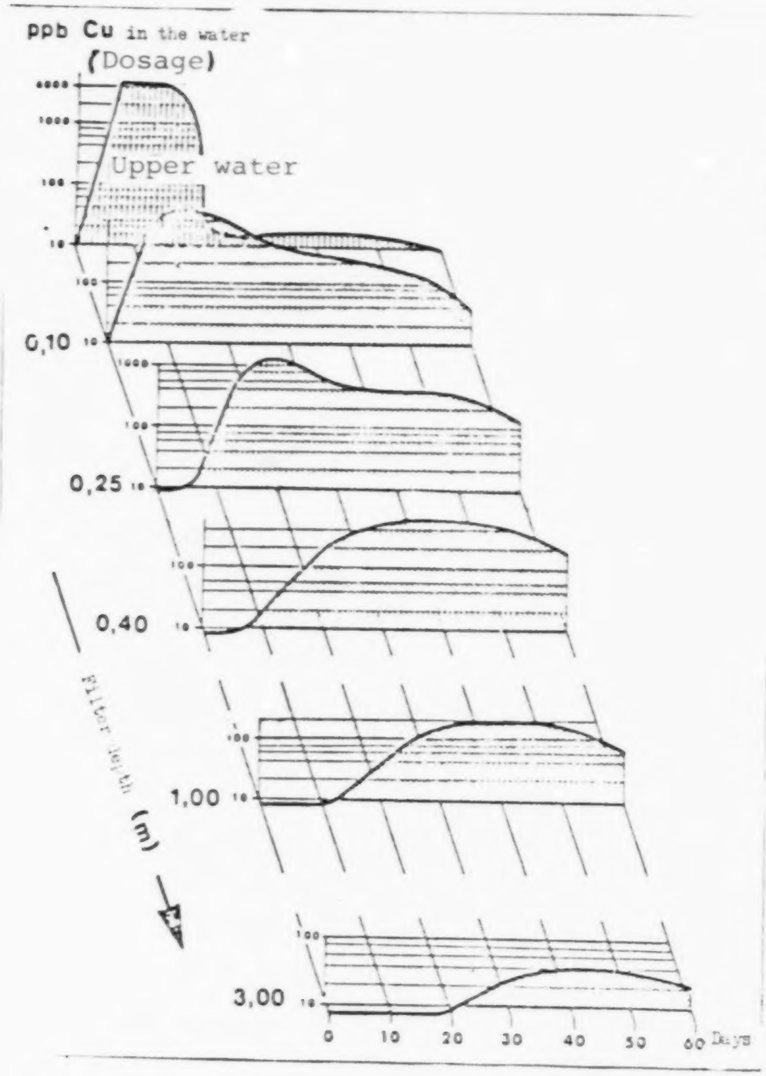


Fig. 11 Behaviour of a sudden loading of copper in slow sand filtration

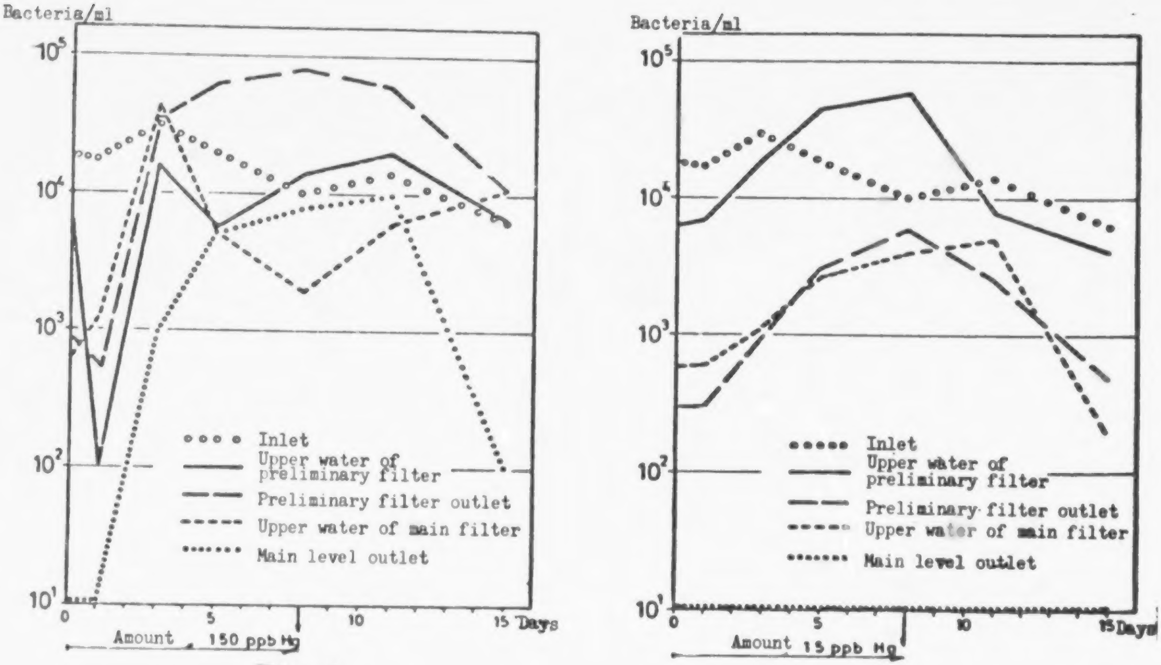
In Table 4 are listed some of the organic substances that have been shown to occur in anaerobic breakdown of algae, their occurrence, and their behaviour in various trials. As the third column shows, most of these materials could also be found in surface water of the Ruhr. The elimination rates in column 4 were different in the slow sand filter model.

The formation of palmitic acid, stearic acid, and methylamine in the upper water of slow sand filters with algal growth could be detected. The last column of the table shows the results of an experiment in which an algal suspension was added to the filter. Palmitic, hexadecatetraenoic, and stearic acids, tyramine, and methylamine were released in such quantities that their concentration in the filter discharge was even higher than in the upper water (7).

On the addition of many heavy metals a clear stimulation of the bacterial activity could be observed. Fig. 12 shows the variation of the colony counts for two experiments in which mercury was added in different concentrations (8). In the case of the lower mercury loading the increase of the bacterial count in the upper water of the filter can be seen in the right-hand half of the figure, together with the increased bacterial content in the discharge from the preliminary filter. The discharge from the main filter shows no reaction, but a reaction can be clearly seen in the left-hand half of Fig. 12, relating to 10-times greater mercury loading. In the upper water of the preliminary filter the bactericidal action of the mercury is here clearly evident, at least in the initial stages.

TABLE 4 Occurrence and behaviour of fatty acids and amines from algae in slow sand filtration

	Release on algal degradation in vitro (anaerobic)	Detection in the Ruhr water +∼<1 ug/l ++∼1-20 ug/l	Elimination on slow sand filter model Model expt. with high loading	Concentration increase in upper water of filter due to algal excretion	Concentration increase in filter due to degradation in filter discharge in the case of loading with algal cells
Palmitic acid	+	++	30 - 60 %	(+)	+
Hexadecatetraenoic acid	++	+	0 %	-	++
Stearic acid	+	+	30 - 50 %	+	+
Linolenic acid	++	++	0 %	-	-
Cadaverine	++	NN	99,5 %	-	-
Putrescine	++	(+)	99,0 %	-	-
Tyramine	++	NN	0 %	-	++
Methylamine	+	++	50,0 %	+	++



Filter A

Filter C

Fig. 12 Effect of loading with mercury on the bacterial count in the preliminary gravel filter and the main sand filter system

Fig. 13 shows that small additions of indole and skatole are eliminated in the preliminary filter after a running-in time of a few days (9). At the same time a fall of the oxygen content in the preliminary filter discharge is observed, which cannot be explained by degradation of the organic substances added. Their complete oxidation would have required less than 0.5 mg O_2/l. A stimulating action on other mineralization processes must therefore be assumed.

Polarographic determination of the heavy metals with maintenance of definite pH permits a differentiation of heavy metals bound stably and weakly in complexes (Fig. 14). As the pH decreases, increasing amounts of heavy metals are detectable in the Ruhr water (10).

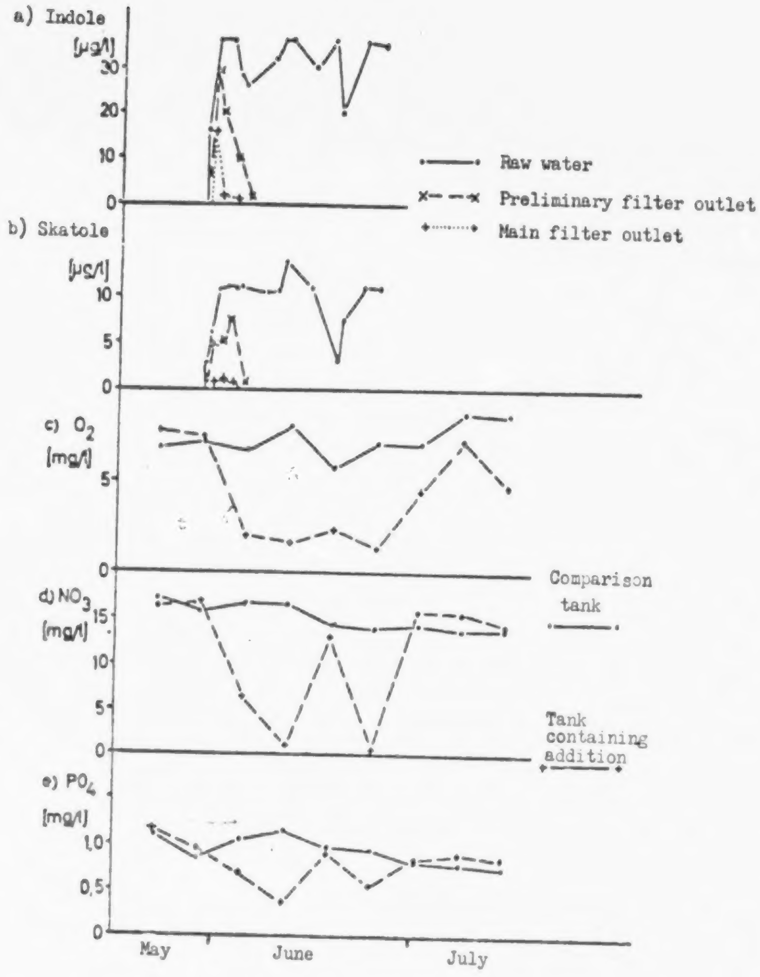


Fig. 13 Addition and elimination of a) indole and b) skatole in two-stage slow filtration, and c) O_2^-, d) NO_3^-, and e) PO_4 - contents in the preliminary filter outlet

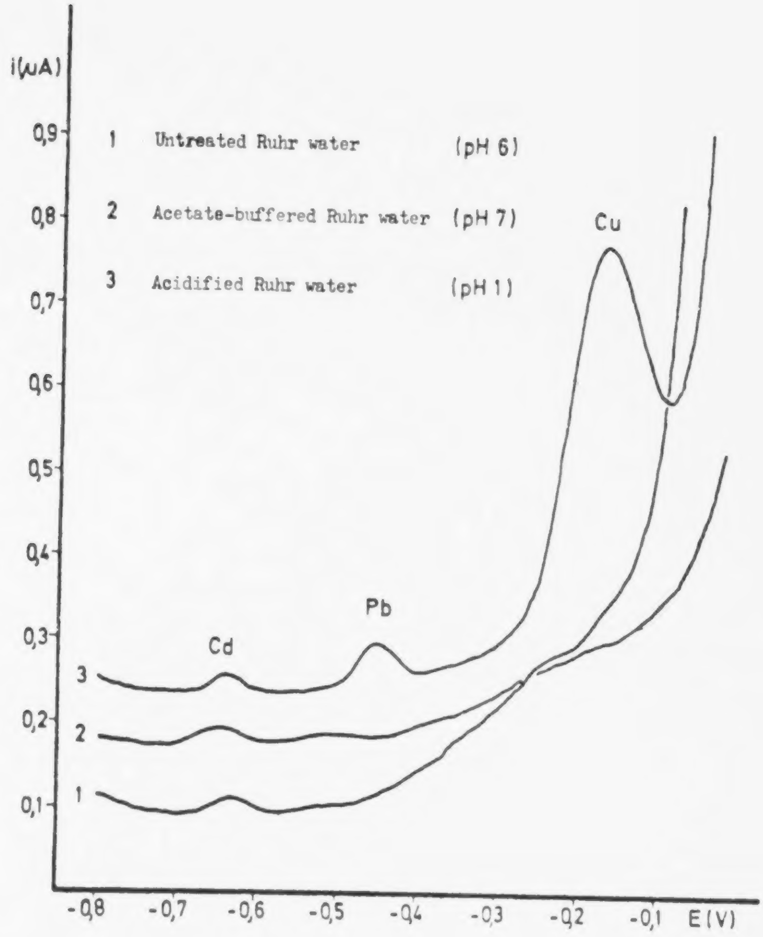


Fig. 14 Determination of labile (Curve 2) and total (Curve 3) Cd-Pb-Cu by means of DPASV. Electrolysis time 180 sec.

According to Table 5, when the loadings of the Ruhr are relatively low, lead is found to be 100% stably bound and cadmium to be 100% labile. Both elements were completely eliminated in a 70 cm long experimental biological column.

Copper and zinc are present in higher concentrations and in both cases only part of the metal is labile. As expected, the labile copper is completely removed in the filtration. Only 50% of the stably complexed copper could be removed.

TABLE 5 Proportions of stably and weakly bound heavy metals in river water and filtrate

		LEAD		COPPER		ZINC		CADMIUM	
		stably bound	labile	stably bound	labile	stably bound	labile	stably bound	labile
Raw water	PPB	1,3	<0,2	14,0	3,5	60,5	49,5	<0,1	0,6
	%	100,0		80,0	20,0	55,0	45,0		100,0
Filtrate	PPB	<0,2	<0,2	7,0	<2,0	<2,0	5,5	<0,1	<0,1
	%	-	-	100,0	-	-	100,0	-	-
Elimination	%	100,0		50,0	100,0	100,0	90,0		100,0

A different situation is observed with zinc. In this case the stably bound fraction is completely removed and the labile fraction only to the extent of 90%. From this it is evident that the stability of the heavy metal complexes does not allow any general rules to be formulated about their elimination. The individual elements behave very differently, according to their type and their concentration (10).

In conclusion, some further indications may be given on the efficiency of continually loaded plants with respect to microimpurities. The investigated water-production plant consists of a preliminary gravel filter, a main sand filter, and a 50-m long soil passage, which is completed in 1-2 days (Fig. 15).

The DOC shown in Fig. 16, measured with Maihak apparatus, is reduced on average by about 50% (11). However, the figure shows clearly that the elimination rate of the organic carbon, contrary to expectations, is better during the winter months than in the summer. This can be explained by loading with biogenic substances from algae.

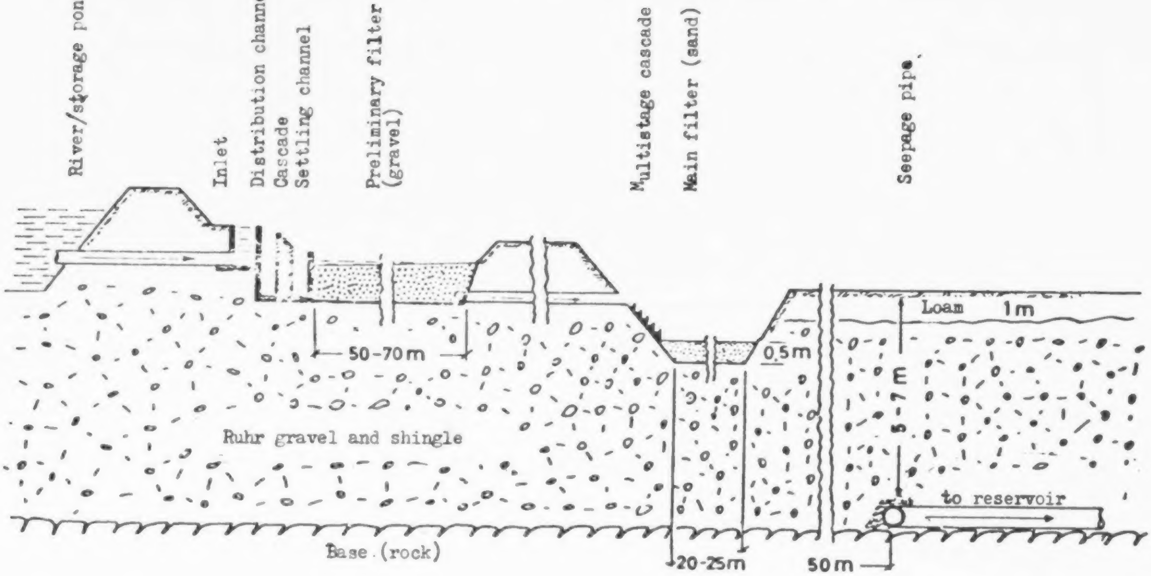


Fig. 15 Artificial ground-water enrichment scheme

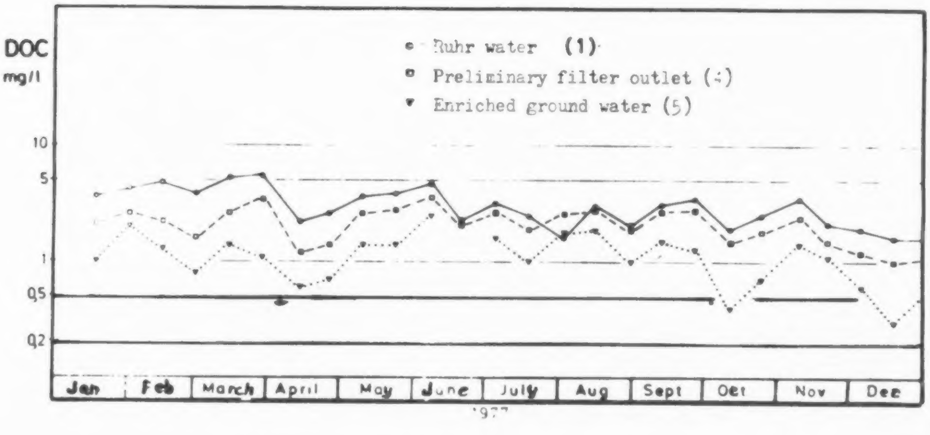


Fig. 16 Elimination of the DOC in artificial ground-water enrichment

Fig. 17 gives the measured elimination of the Ruhr zinc content, which is on average 150 μg/l. The measurements were made in the same system. The mean elimination rate is 92% (12).

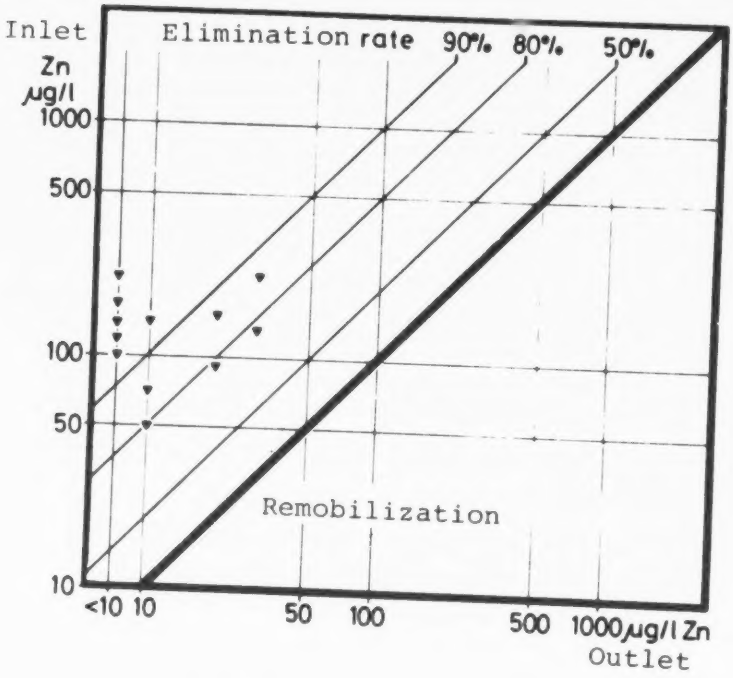


Fig. 17 Preliminary gravel filter, slow sand filter and soil passage (DFG 1/5)

Fig. 18 illustrates the situation for copper, the mean content of which in the raw water was 30 μg/l. In this case the mean elimination was 65%. However, some analytical data clearly lie in the right-hand field. As the copper concentration in the ground water was higher than that in the raw water, the possibility of remobilization processes must be considered.

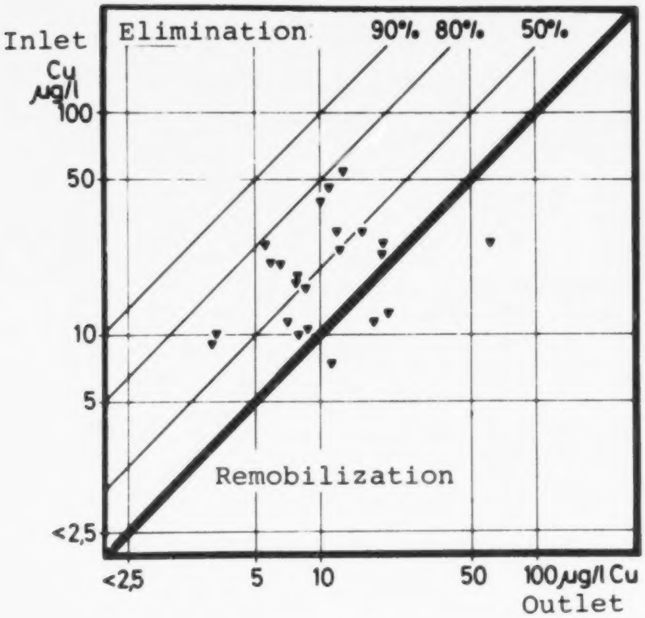


Fig. 18

Preliminary gravel filter, slow sand filter and soil passage (DFG 1/5)

Fig. 19 shows the same situation as a function of time. It can be seen clearly that the poor or even negative results again occur in the summer months, from which it can be deduced with high probability that algal excretion products are involved in these processes (12).

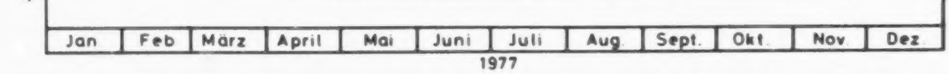


Fig. 19 Elimination of copper in the artificial enrichment of ground water (DFG 1/4/5)

Whereas we have been able to extend considerably our knowledge of the activity of slow sand filters with respect to micro-impurities in recent years, this has given rise to many new problems that require further elucidation.

(1) SCHMIDT, K.H.
Die Abbauleistungen der Bakterienflora bei der Langsamsandfiltration und ihre Beeinflussung durch die Rohwasserqualität und andere Umwelteinflüsse. Biologische Studien zur künstlichen Grundwasseranreicherung
Veröffentl. d. Hydrol. Forschungsabt. der Dortmunder Stadtwerke AG (1963), Nr. 5

(2) STUHLMANN, F.
Studien zum Verhalten stickstoffhaltiger Wasserinhaltsstoffe bei der Langsamsandfiltration
Veröffentl. des Instituts für Wasserforschung GmbH Dortmund und der Hydrol. Abt. der Dortmunder Stadtwerke (1972), Nr. 10

(3) SCHÖTTLER, U.
Schwermetalle und Reinigungsleistung von Langsamsandfiltern
Fachtagung der Deutschen Sektion für Limnologie in der Internationalen Vereinigung für Limnologie, Siegburg 6-10 Okt. 1975

(4) SCHÖTTLER, U.
Das Verhalten von Schwermetallen bei der Langsamsandfiltration
Zeitschrift der Deutschen Geologischen Gesellschaft
126 (1975), 373-384

(5) ZULLEI, N.
Polychlorbiphenyle - Literatur - Analytik - Langsamsandfiltration
Veröffentl. des Instituts für Wasserforschung GmbH Dortmund und der Hydrol. Abt. der Dortmunder Stadtwerke AG (1977), Nr. 24

(6) BAUER, U.
Über das Verhalten von Bioziden bei der Wasseraufbereitung - unter besonderer Berücksichtigung der Langsamsandfiltration
Veröffentl. des Instituts für Wasserforschung GmbH Dortmund und der Hydrol. Abt. der Dortmunder Stadtwerke AG (1972) Nr. 15

(7) KLEIN, G.
Studie zum Verhalten von Algenabbauprodukten bei der Langsamsandfiltration
(in preparation)

(8) SCHÖTTLER, U.
Natürliche Filtrationssysteme und Schwermetalle, aufgezeigt am Beispiel von Quecksilber und Cadmium
J. Vom Wasser 49 (1977), 295-313

(9) KLEIN, G.
Die Bildung von Tryptophanmetaboliten beim anaeroben Abbau von Algen und deren Bedeutung für Gewässer und Wassergütewirtschaft
Z. f. Wasser- und Abwasserforschung 9 (1976), 2, 55-59

(10) NÄHLE, C.
Zwischenbericht 1978 zum KfW-Forschungsvorhaben C.00-4.01/78 "Untersuchungen über den Einfluß biogener und anthropogener Komplexbildner auf natürliche Filtrationssysteme" (1978)

(11) SCHÖTTLER, U.
Abschlußbericht zum DFG-Forschungsvorhaben Schm 294-12 "Das Verhalten von Spurenmetallen bei der Wasseraufbereitung unter besonderer Berücksichtigung der künstlichen Grundwasseranreicherung"

(12) SCHÖTTLER, U.
Die Aufbereitung von schwermetallbelastetem Oberflächenwasser durch Langsamsandfilter
11. Essener Tagung, 8-10 März 1978 (in press)

REMOVAL OF TRACE CONTAMINANTS FROM RECLAIMED WATER DURING AQUIFER PASSAGE

P.V. Roberts

In the arid Western regions of the U.S.A., reclamation and reuse of wastewater is assuming an increasingly important role in planning to meet future water supply needs. Potable reuse of highly treated reclaimed waters is among the alternatives being considered. Potential health risks posed by trace organic and inorganic micropollutants as well as pathogens are difficult to evaluate.

Because of these risk factors, public health officials in California require that reclaimed water may not be used directly as a potable supply but rather only by the indirect route of groundwater recharge. Water for potable reuse must be treated by granular activated carbon with an empty bed contact time of at least 30 minutes. The treated water must then be introduced into the groundwater either by percolation from the surface through the vadose zone or by direct injection into a confined aquifer. It must be demonstrated that the reclaimed water has resided in the groundwater zone for a minimum of one year prior to extraction for potable reuse.

In view of the public health risks entailed by potable reuse, the authorities certainly are justified in their cautious stand that requires groundwater passage prior to potable reuse. Water quality benefits anticipated to result from passage through an aquifer include :

(1) reducing the concentrations of contaminants, and (2) damping concentration fluctuations so as to decrease the frequency of extreme high values. Unfortunately, data are lacking to help us evaluate what degree of quality assurance is provided. Particularly for the organic and inorganic micropollutants that are suspected of having chronic toxic or carcinogenic effects, little is known regarding elimination or retention in aquifers.

This research was undertaken to answer questions concerning the contribution of aquifer passage to improving the reliability of a water reclamation system. Investigations of the transformations and fates of trace contaminants, especially organic micropollutants, are emphasized. Specific objectives include the following:

1. To determine the extent to which trace contaminants are removed during aquifer passage.
2. To identify the processes responsible for removal, e.g. biodegradation, adsorption, ion exchange, chemical oxidation, or precipitation.
3. To quantify the rate of transport of trace contaminants relative to the rate of movement of injected water.
4. To estimate the field retention capacity of the aquifer with respect to individual trace contaminants, where processes such as adsorption or ion exchange are believed responsible for removal.

Experimental Methods

Reclamation Facility

The data presented herein are based in large part on field studies carried out at the Palo Alto Reclamation

Facility. This facility consists of a water reclamation plant and a well field for groundwater recharge (1). The hydraulic capacity is 0.09 m^3/s.

The water reclamation plant is an advanced treatment facility based on the concept of physical-chemical treatment. The unit operations include high lime addition, coagulation, and sedimentation; ammonia removal by surface aeration; ozonation; granular activated-carbon treatment; mixed-media filtration; and disinfection with chlorine. The anticipated quality of influent and effluent is summarized in Table 1.

During the observation period from which the data in this paper are drawn, the reclamation plant was operated in a start-up mode. Treatment consisted of lime treatment at pH 9, air stripping, and recarbonation, followed by ozonation and sand filtration. The ozone dose was approximately 50 mg/l. Owing to the absence of activated-carbon treatment, the organic quality of the effluent was not as good as anticipated for the full treatment sequence. The average COD concentration in the effluent was 20 mg/l.

The full-scale injection/extraction well field is composed of a network of 9 injection wells, 9 extraction wells, and 62 monitoring wells in an area approximately 3 kilometers long by 1 kilometer wide. The wells are intended for recharge and removal of water in an aquifer approximately 12 to 15 m below the ground surface and 1 to 3 m thick.

Pilot Experiment

A pilot experiment was conducted at a test well from August to November 1977 to gain experience with direct

TABLE 1 Projected quality of reclamation plant effluent based on present Palo Alto secondary effluent average characteristics and results of treatment studies (2)

	Present Palo Alto Secondary Effluent Average Characteristics	Projected Characteristics of Reclamation Plant Effluent
COD, mg/l	53	6
MBAS, mg/l	0.12	0.05
Nitrogen, mg/l as N		
NH_3	24	2
NO_2^-	0.3	0.3
NO_3^-	0.4	0.4
Organic	3.0	0.5
Total	27.7	2.7
Heavy metals, µg/l		
Cd	2.5	<0.1
Zn	5	1.5
Cu	49	<5
Fe	3	<1
Ag	2.3	<0.5
Mineral characteristics, mg/l		
Sodium	162	162
Potassium	11	11
Calcium	43	117
Magnesium	15	2
Chloride	204	262
Sulfate	85	85
Bicarbonate	249	216
Hardness, mg/l as $CaCO_3$	169	300
Alkalinity, mg/l as $CaCO_3$	204	177
Total Dissolved Solids, mg/l	668	771

injection of reclaimed water prior to beginning injection and extraction at full scale. The test site for the pilot experiment is shown schematically in Figure 1. Reclaimed water was injected into the recharge aquifer through Well 12. Wells P1 through P4 are sampling piezometers completed in the same aquifer, located approximately 8 m from the injection well. From core samples and drawdown test results, it was concluded prior to the commencement of injection that the injected water would flow preferentially in the direction of Well P4. A drawdown test at Well 12 indicated an average transmissivity of $7 \times 10^{-5} m^3/m.s$ based on the assumption of radial flow, but the transmissivity value in the direction of P4 is believed to be substantially greater. The porosity of a core sample from Well P4 was 0.22.

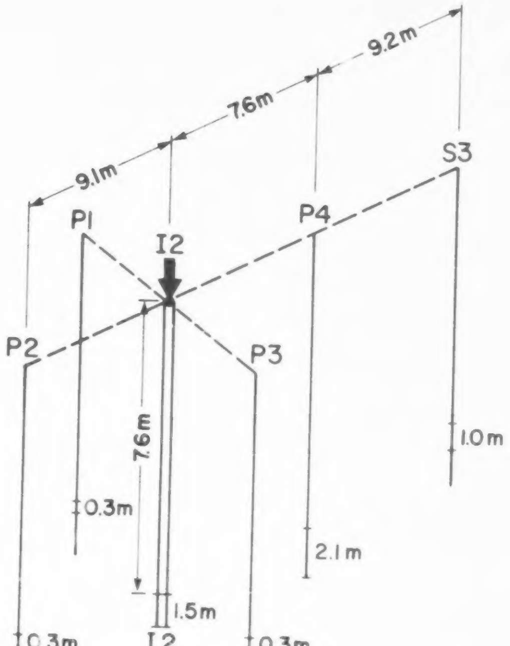


Fig. 1 Injection and observation well arrangement for pilot study. I2 is the injection well; P1, P2, P3, P4, and S3 are observation wells

Analytical Methods

Highly volatile organic substances were analyzed using a head space analysis technique (3). Compounds determined by this method included halogenated aliphatics containing one and two carbon atoms.

Moderately volatile compounds were determined using a closed-loop stripping procedure (4). Concentration of the organic solutes was achieved by circulating air for a period of two hours through a loop that passed through the 500-ml sample and a 1-mg activated-carbon adsorption trap. The adsorbed organic substance was then eluted with carbon disulfide. The extracts were separated by gas chromatography on a 20 m UCON HB5100 glass capillary column using a Carlo Erba gas chromatograph with flame ionization detector. Quantification was based on comparison with 1-Cl-C_8, 1-Cl-C_{12}, and 1-Cl-C_{16} internal standard peaks. Identification of peaks was achieved by means of a Finnigan Model 4000 gas chromatograph-mass spectrometer.

Trace metals were determined by flameless atomic absorption spectrophotometry (Perkin Elmer 403) following APDC chelation and methyl isobutyl ketone extraction of unfiltered, acid-preserved samples.

Interpreting Field Data

The experiment described is equivalent in principle to imposing a step change in the composition of fluid at the injection point. Prior to injection, the water in the aquifer was relatively homogeneous. As injection proceeded, the formation groundwater was displaced outward from the injection point toward and past the observation wells, resulting in concentration changes at the sampling points.

Estimating the Rate of Transport and the Field Retention Capacity

The rate of transport and field retention capacity for a specific pollutant can be estimated from observations of the concentration history at an observation point following a step change in concentration at the injection point (5). The approach is premised on analogy to chemical reactor analysis (6). The aquifer is treated as a reactor of arbitrary shape and volume. The effective pore volume of the aquifer element is evaluated from the integral

$$V_p = \int_o^\infty (1 - f_{IW})\ dV_{IW} \qquad (1)$$

where V_p is the effective pore volume in m^3, f_{IW} the fractional breakthrough of injection water as measured by a conservative tracer, and V_{IW} is the volume of water injected in m^3. The field retention capacity of the aquifer with respect to pollutant i is given by

$$r_i = \frac{(\overline{C}_o)_i \int_o^\infty (f_{IW} - f_i)\ dV_{IW}}{\frac{1}{\varepsilon_{aq}} \int_o^\infty (1 - f_{IW})\ dV_{IW}} \qquad (2)$$

where r_i is the specific retention capacity in g of component i retained per m^3 aquifer; $(\overline{C}_o)_i$ is the average concentration of i in the injected water, g/m^3; f_i is the fractional breakthrough of component i , a dimensionless function of the injected volume; and ε_{aq} is the effective porosity of the aquifer element. The ratio of the average transport velocity of a pollutant to that of water is derived from a mass balance for the aquifer element:

$$\frac{U_i}{U_{H_2O}} = \frac{\int_0^{\infty} (1 - f_{IW}) \; dV_{IW}}{\int_0^{\infty} (1 - f_i) \; dV_{IW}} \tag{3}$$

where U_{H_2O} is the average velocity across the aquifer element boundary in m/s ; and U_i is the corresponding velocity of pollutant i.

Identifying Transformation Processes from Field Data

The concentration response at an observation well can be interpreted to identify the processes affecting the transport of a pollutant. Several types of concentration responses are illustrated in Figure 2. A conservative tracer that does not interact within the aquifer will appear as a sharp concentration front in the absence of dispersion, or as an S-shaped wave if dispersion is significant (6,7). A solute which is adsorbed in the aquifer will be delayed compared to the conservative tracer, and the length of the concentration front will be extended. The concentrations of conservative as well as sorbing solutes eventually reach the upper limit imposed by the concentration in the injection water, at which point breakthrough is complete. If a solute is biodegradable under the conditions in the aquifer, its concentration may first rise until a population of microorganisms has developed that is capable of metabolizing it after this acclimatization period; the concentration may then decline to a steady-state level, as shown in Figure 2.

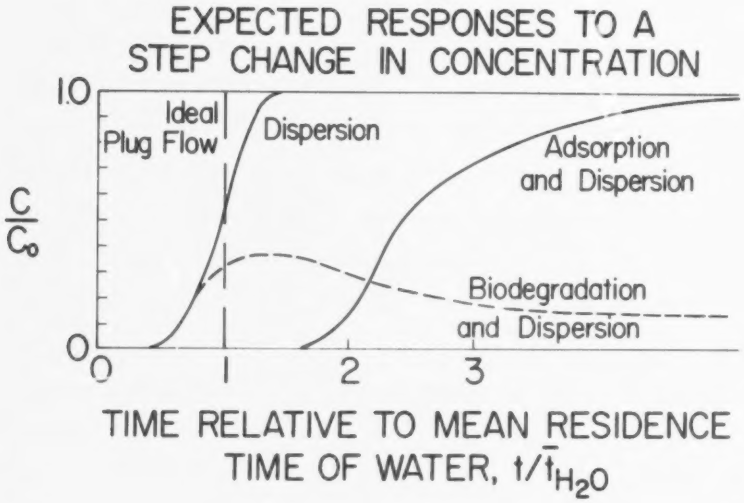


Fig. 2 Forms of response to a step-change concentration stimulus

Hence, processes such as adsorption or biodegradation that may transform a solute or attenuate its movement can be identified by comparing the concentration response to that of a conservative tracer and to the typical forms such as those in Figure 2.

Results

Breakthrough of Injected Water

The rapid appearance of water of low salinity at Observation Well P4 proved the existence of a good hydraulic connection between this well and the injection well, confirming the expected preferential flow in the direction of Well P4 compared to other directions. Hence, monitoring of trace contaminants was limited to Well P4 to the exclusion of the other observation wells.

The breakthrough of injected water was calculated from conductivity measurements. The correlation coefficient between conductivity and chloride was 0.967 for 17 paired values, which is significant at the 99.99-percent level.

The breakthrough at the observation well commenced within the first 10 m^3 injected volume, reached a fractional value of 0.50 at 35 m^3 injected volume, and was virtually complete after 200 m^3 had been injected (Figure 3). The effective pore volume of the aquifer element defined by Well P4 is 45 m^3, evaluated from the integral in Figure 3. The average residence time in the aquifer element is approximately 12 hours, at an average injection rate of one liter per second.

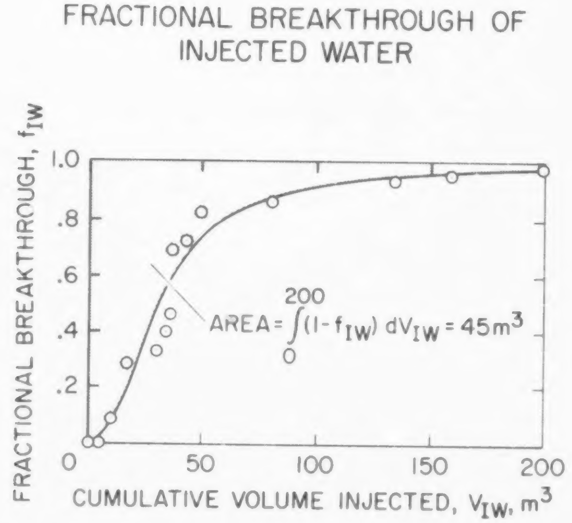


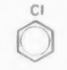
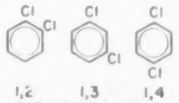
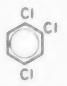
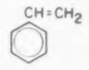
Fig. 3 Breakthrough of injected water at observation well P4

Concentrations of Organic Micropollutants

The injection water contained measurable amounts of residual organic micropollutants that were not removed in treatment. An overview of the compounds regularly quantified in the injection water at concentrations exceeding 100 ng/l is presented in Table 2. Their large number may be explained by the fact that the water did not receive activated-carbon treatment during this period of observation. Subsequent observations after commencement of activated-carbon treatment have shown that substantially lower concentrations of organic micropollutants are attained compared to the values reported here.

TABLE 2

COMPOUNDS REGULARLY QUANTIFIABLE IN INJECTION WATER
CRITERION $C_{IW} > 100$ ng/ℓ

CLOSED LOOP STRIPPING ANALYSIS	HEAD SPACE ANALYSIS
CHLORINATED AROMATIC COMPOUNDS  CHLOROBENZENE  1,2 1,3 1,4 DICHLOROBENZENE ISOMERS  1,2,4 TRICHLOROBENZENE AROMATIC HYDROCARBONS  STYRENE NAPHTHALENE ARYL AND ALKYL CYANIDES BENZONITRILE ALSO C_5 TO C_9 ALKYL CYANIDES $C_nH_{2n+1}CN$	TRIHALOMETHANE COMPOUNDS $CHCl_3$ CHLOROFORM $CHCl_2Br$ BROMODICHLOROMETHANE $CHClBr_2$ DIBROMOCHLOROMETHANE $CHBr_3$ BROMOFORM OTHER CHLORINATED ALIPHATIC COMPOUNDS $Cl_2C{=}CHCl$ TRICHLOROETHYLENE $Cl_2C{=}CCl_2$ TETRACHLOROETHYLENE Cl_3CCH_3 1,1,1-TRICHLOROETHANE

Aromatic Compounds

Data for aromatic and substituted aromatic hydrocarbons are summarized in Table 3. From gas chromatographic results it is apparent that a small number of compounds predominate in the injection water (Figure 4). The sources of chlorinated benzene compounds are believed to be industrial solvent wastes, while benzonitrile is thought to be present in electroplating wastes. Heptaldehyde and styrene may be products of ozonation and chlorination in the reclamation plant (8).

The concentrations of organic micropollutants analyzed by closed-loop stripping analysis were near or below their respective detection limits at the observation well shortly after injection began (Table 3). The concentrations of some compounds rose appreciably during the course of the experiment, as exemplified by chlorobenzene, styrene, and benzonitrile. During the final

TABLE 3

CONCENTRATIONS OF AROMATIC AND SUBSTITUTED AROMATIC MICROPOLLUTANTS

	CONCENTRATIONS, ng/ℓ				
	INJECTED WATER		OBSERVATION WELL		
	ENTIRE PERIOD; V=0 TO 4500 m^3		V_{IW}=0 TO 500 m^3 (n=5)	V_{IW}=3000 TO 4500 m^3 (n=5)	
	LOG MEAN	95% CI FOR MEAN (n=9)	LOG MEAN	LOG MEAN	95% CI FOR MEAN
CHLOROBENZENE	4,130	1,480 TO 11,500	150	3,380	2,620 TO 4,370
1,3-DICHLOROBENZENE	630	255 TO 1,550	< 15	80	50 TO 120
1,4-DICHLOROBENZENE	530	265 TO 1,060	< 15	100	70 TO 150
1,2-DICHLOROBENZENE	1,940	1,160 TO 3,250	< 15	460	330 TO 630
1,2,4-TRICHLOROBENZENE	150	38 TO 590	< 15	< 15	—
NAPHTHALENE	910	320 TO 2,540	70	60	40 TO 85
STYRENE	1,000	500 TO 2,000	< 15	2,150	1,600 TO 3,000
HEPTALDEHYDE	11,700	9,500 TO 14,500	< 75	< 75	—
BENZONITRILE	5,500	3,300 TO 8,900	<400	2,030	1,500 TO 2,700

third of the observations, the concentrations of chlorobenzene and styrene were not significantly different from their respective concentrations in the injected water, as demonstrated by the overlap of the 95 % confidence intervals for the mean (95 % CI in Table 3). This is taken as an operating definition of "complete breakthrough."

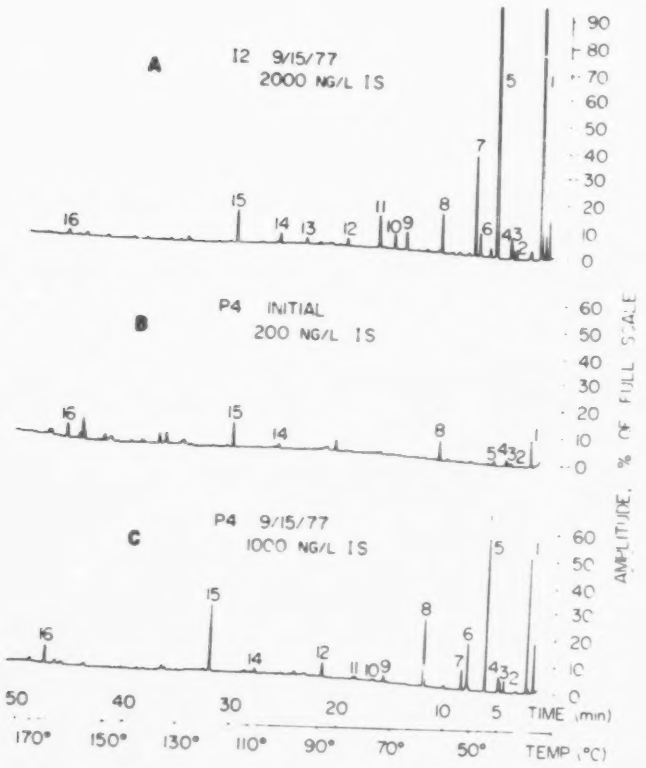


Fig. 4 Gas-chromatographic analyses of injected water and observation well samples

Substances identified are: (1) toluene + tetrachloroethylene; (2) ethylbenzene; (3) p-xylene; (4) m-xylene; (5) chlorobenzene with trace of o-xylene; (6) unknown y; (7) sturene + unknown; (8) ClC_8 (Internal Standard); (9) 1,3-dichlorobenzene; (10) 1,4-dichlorobenzene; (11) 1,2-dichlorobenzene; (12) benzonitrile; (13) 1,2,4-trichlorobenzene; (14) naphthalene; (15) $Cl\text{-}C_{12}$ (Internal Standard); (16) $Cl\text{-}Cl_{16}$ (Internal Standard)

The concentration response of chlorobenzene is plotted in Figure 5 in a form suitable for estimating the field retention capacity and the relative transport velocity. According to Eq. 2, the field retention capacity for chlorobenzene is

$$\left\{\frac{\overline{C_o}\ {}_{o}\!\int^{\infty} (F_{IW} - f_i)\ dV_{IW}}{\frac{1}{\varepsilon_{aq}}\ {}_{o}\!\int^{\infty}(1 - f_{IW})\ dV_{IW}}\right\} = \frac{0.0041\left[\frac{g}{m^3}\right] \times 1580\left[m^3\right]}{\frac{1}{0.22} \times 45\left[m^3\right]}$$

$$= 0.032 \text{ g chlorobenzene retained per } m^3 \text{ aquifer}$$

and the ratio of the transport velocity to that of water according to Eq. 3 is

$$\frac{u_{C_6H_5Cl}}{u_{H_2O}} = \frac{45}{1625} = 1/36$$

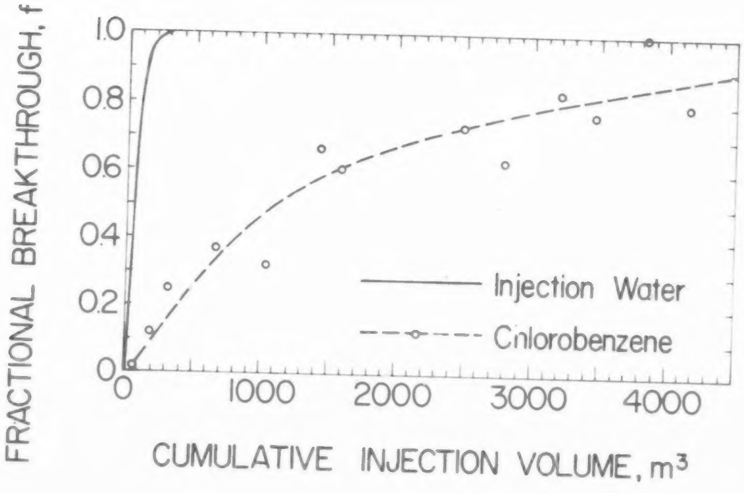


Fig. 5 Response of chlorobenzene concentration to a step-change stimulus

Halogenated Aliphatic Compounds

Data for the components analyzed by head space analysis are shown in Table 4. During the early portion of the experiment ($V_{IW} < 200\ m^3$) the concentrations at the observation point were reduced to less than the detection limit for all components. Breakthrough was observed at a point corresponding to 1000 m^3 injected volume or less. For all compounds, the 95 % confidence limits for concentrations at the observation well during the period embracing injected volume between 1000 m^3 and 1500 m^3 overlap those for the injected water. Unfortunately the confidence limits are quite broad, owing to the variability of the analyses and the small number of samples. Only the data for chloroform are sufficiently reliable to permit interpretation in the form of a breakthrough response (Figure 6). It appears that the midpoint of the chloroform breakthrough is reached at approximately 200 m^3 injected volume. The breakthrough appears to be virtually complete by 1000 m^3 injected volume. The rate

TABLE 4 Concentrations of halogenated aliphatic micropollutants

	CONCENTRATIONS, μg/ℓ				
	INJECTED WATER		OBSERVATION WELL		
	V_{IW}=0 TO 1500m^3 (n=6)		V_{IW}=0 TO 200m^3 (n=3)	V_{IW}=1000 TO 1500m^3 (n=3)	
	LOG MEAN	95% CI FOR MEAN	LOG MEAN	LOG MEAN	95% CI FOR MEAN
CHLOROFORM	3.3	1.9 TO 5.8	<0.1	4.3	3.9 TO 4.7
1,1,1-TRICHLOROETHANE	2.7	0.63 TO 11.5	<0.1	7.1	5 TO 10
TRICHLORETHYLENE	9.9	4.1 TO 24	<0.1	5.4	3.3 TO 8.8
BROMODICHLOROMETHANE	1.1	0.3 TO 4.3	<0.1	1.5	1.1 TO 2.1
TETRACHLOROETHYLENE	0.5	0.12 TO 2	<0.1	0.22	0.033 TO 1.4
DIBROMOCHLOROMETHANE	5.1	2 TO 13	<0.1	0.3	0.02 TO 4
BROMOFORM	3.3	0.33 TO 33	<0.1	0.8	0.06 TO 10

of transport of chloroform can be approximated only very roughly. The best estimate of the ratio of the chloroform transport velocity to the velocity of water movement is

$$\frac{u_{CHCl_3}}{u_{water}} = \frac{45}{45 + 200} \cong \frac{1}{5}$$

evaluated from Eq. 3. The field retention capacity for chloroform is

$$\frac{0.0033\left[\frac{g}{m^3}\right] \times 200\ [m^3]}{\frac{1}{0.22} \times 45\ [m^3]} = 0.0032 \left[\frac{\text{g chloroform retained}}{m^3 \text{ aquifer}}\right]$$

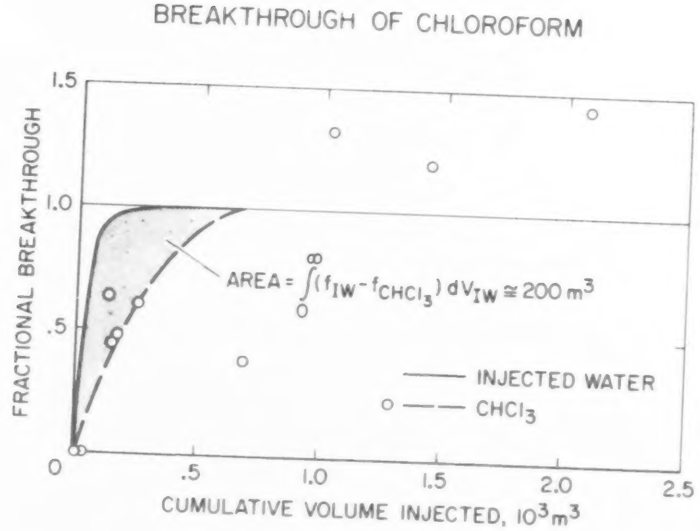


Fig. 6 Response of chloroform to a step-change stimulus

Biodegradation of Individual Organic Compounds

The behavior of naphthalene exhibited strong evidence of the influence of biodegradation (Figure 7). The concentration rose significantly above the background value during the period following the breakthrough of injected water. The concentration exceeded 100 ng/l in the range between 40 m^3 and 1500 m^3 injected volume, exceeding 10 percent of the average injected concentration throughout that range. A peak concentration of 900 ng/l, approximately equal to the average injected concentration, was reached at an injected volume of 680 m^3. After 1500 m^3 injected volume, the concentration decreased below 10 percent of the average injected concentration for the remainder of the observations. This decrease cannot be explained by a secular decrease in the concentration in the injected water.

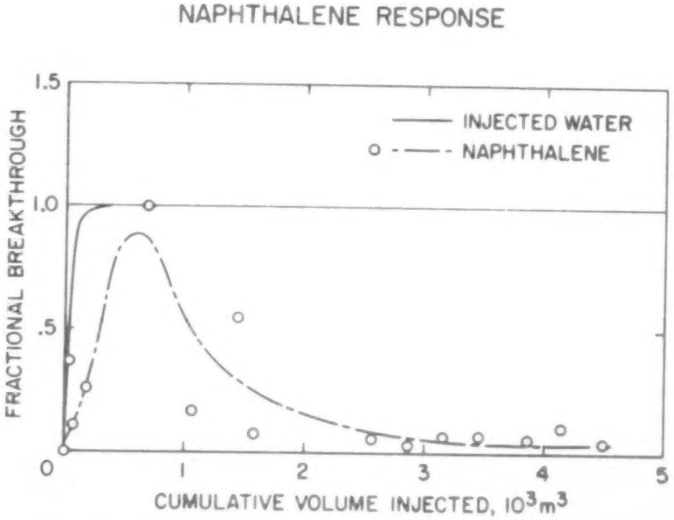


Fig. 7 Response of naphthalene

A plausible explanation for the decline in naphthalene concentration at the observation well is that the rate of biodegradation was enhanced by the development of a population of microorganisms capable of metabolizing styrene. It is hypothesized that acclimation occured during the initial breakthrough of naphthalene. The onset of biodegradation after an initial lag period is commonly observed in degradation studies. Furthermore, it has been postulated that substrates will be degraded in natural systems to the point at which a low, steady-state concentration is reached (9). McCarty (9) estimated the steady-state concentrations of acetate and glucose after an infinite residence time in an aerobic environment to be 25 x 10^{-8} mol per liter and 13 x 10^{-8} mol/liter, respectively. These conditions correspond to the open ocean or large oligothrophic lakes.

The steady-state concentration of naphthalene observed in the groundwater environment in this work is 0.47 x 10^{-9} ± 0.17 x 10^{-9} mol per liter. Hence, the value for naphthalene is two to three orders of magnitude lower than expected for more readily degradable substrates such as acetate and glucose. From this comparison it can be hypothesized that the groundwater zone constitutes an environment especially amenable to biodegradation.

It is possible that biodegradation also was responsible for the removal of heptaldehyde. However, the field data provide no confirming evidence in the form of a concentration peak followed by a decline to a low, steady-state concentration. Since heptaldehyde is believed to be readily degradable, it is conceivable that the acclimatization of microorganisms occured within the time frame of the breakthrough of injected water.

It might be suspected that the time of travel between the injection and observation points, i.e. approximately 12 hours, was too short for biodegradation of poorly degradable substrates to occur. Concentrations of organic micropollutants were determined before and after a 25-day "rest period" during which no water was injected into the aquifer (Table 5). Since hydrogeologic studies showed no evidence of regional flow in the aquifer, it can be assumed that essentially the same water was sampled at the beginning and end of the period. Of the eight compounds analyzed, the concentrations of six appeared to decrease, while two others increased. Because only a single pair of measurements was made, no statistical conclusions can be reached. It is believed that only changes by a factor greater than two can be considered significant. Only the decrease in the concentration of styrene, which amounts to a tenfold change, is thought to be significant. Biodegradation is a plausible explanation for the disappearance of styrene (10).

TABLE 5 CONCENTRATION CHANGES OF ORGANIC MICROPOLLUTANTS DURING A 25-DAY RESIDENCE PERIOD

	CONCENTRATIONS, μg/l		CHANGE, PERCENT
	INITIAL	AFTER 25 DAYS	
CHLOROFORM	2.4	2.7	+ 12
TRICHLOROETHANE	2.3	2.2	- 4
TRICHLOROETHYLENE	3.3	3.1	- 6
TETRACHLOROETHYLENE	1.8	1.1	-40
CHLOROBENZENE	2.4	1.7	-30
1,2-DICHLOROBENZENE	0.38	0.18	-47
STYRENE	2.1	0.15	-93
NAPHTHALENE	0.035	0.05	+40

Chloroform, trichloroethylene, tetrachloroethylene, chlorobenzene, 1,2-dichlorobenzene, and naphthalene were not degraded to a significant extent under the conditions of this experiment. However, it must be borne in mind that the conditions were anoxic, less than 0.5 mg/l dissolved oxygen.

Moreover, the concentration of naphthalene at the sampling point was very low, corresponding to the steady-state level that presumably represents the lower limit attainable by biodegradation. Hence, it may not be inferred from these data that the substances in question would not be degraded in other situations in which their concentrations were higher and sufficient oxygen were present.

Dissolved Oxygen and Organic Collective Parameters

Dissolved oxygen, COD, and TOC were determined in paired samples from the injection well head and Well P4 (Table 6). There was a consistent decrease in dissolved oxygen concentration between the injection well and Well P4. The injected water was saturated with oxygen, having an average concentration of 8 mg/l. Samples from Well P4 consistently showed an oxygen concentration less than 0.5 mg/l. The disappearance of dissolved oxygen coincided with a decrease in the COD concentration of the same magnitude (Table 6).

From this agreement it can be inferred that aerobic degradation of organic substances occurred during the period of residence in the aquifer. The concentration of total organic carbon indicates that the biodegradation must have been relatively complete. The ratio of the COD

TABLE 6 DECREASE IN CONCENTRATIONS OF DISSOLVED OXYGEN AND COLLECTIVE ORGANIC PARAMETERS DURING AQUIFER PASSAGE

	DECREASE BETWEEN INJECTION AND OBSERVATION WELLS		NUMBER OF PAIRED OBSERVATIONS
	MEAN	STD. DEV.	
DISSOLVED OXYGEN, mg/ℓ O_2	8.5	—	—
COD, mg/ℓ O_2	8.8	5.5	16
TOC, mg/ℓ C	3.4	2.1	13
(Δ COD)/(Δ TOC)	2.6	—	—

decrease to that for TOC corresponds to the range of 2.5 to 3.5 expected when organic substances present in wastewater are completely oxidized to end-products such as CO_2 and H_2O (11). However, the data are insufficiently precise to permit a firm conclusion in this regard.

It is unlikely that the observed reduction in the concentrations of COD and TOC resulted from the removal of particulate organic material. The turbidity of the injected water was less than 2 FTU.

Removal of Trace Metals

Concentrations of trace metals are summarized in Table 7. Ag and Cu were removed during aquifer passage throughout the observation period. Cd and Pb were removed during the early part of the period, but concentrations at the observation well were not significantly different from those in the injected water at the end of the period. The concentration of As was higher at the observation well than at injection point throughout the experiment, possibly owing to dissolution or desorption of As from the aquifer minerals.

TABLE 7

REMOVAL OF TRACE METALS DURING AQUIFER PASSAGE

	CONCENTRATIONS, $\mu g/l$				
	INJECTED WATER, MEAN ± STD DEV FOR ENTIRE PERIOD	5 SAMPLES DURING EARLY PART OF PERIOD V = 0 TO $500 m^3$ INJECTED		5 SAMPLES DURING LATTER PART OF PERIOD V = 3000 TO $4500 m^3$ INJECTED	
		MEAN	STD. DEV.	MEAN	STD. DEV.
Ag	2.0 ± 1.6	< 0.5	—	< 0.5	—
As	1.2 ± 0.7	15	5.4	12	2.5
Cd	2.0 ± 0.8	1.0	0.9	1.6	1.7
Cu	102 ± 24	4.4	3.7	28	3.2
Pb	1.3 ± 1.0	0.6	0.2	1.6	0.7

The breakthrough of Cd and Cu are compared to that for the injected water in Figure 8. The fractional breakthrough of Cu reached a value of approximately 0.3 at the end of the experiment after 4500 m^3 had been injected. Hence the rate of transport for Cu is estimated to be less than one-hundredth as great as the rate of movement of the water through the aquifer. The breakthrough of Cd is more rapid, the midpoint being reached within an injected volume of 1500 m^3. The rate of Cd transport is estimated to be approximately one-fortieth as rapid as that of water movement.

Adsorption is the probable mechanism for trace metal removal in the aquifer. The field retention capacity for Cd is calculated to be 17 mg Cd retained per m^3 aquifer. Since the breakthrough of Cu was incomplete, we can only evaluate a lower limit for the field capacity, approximately 2 g Cu per m^3 aquifer.

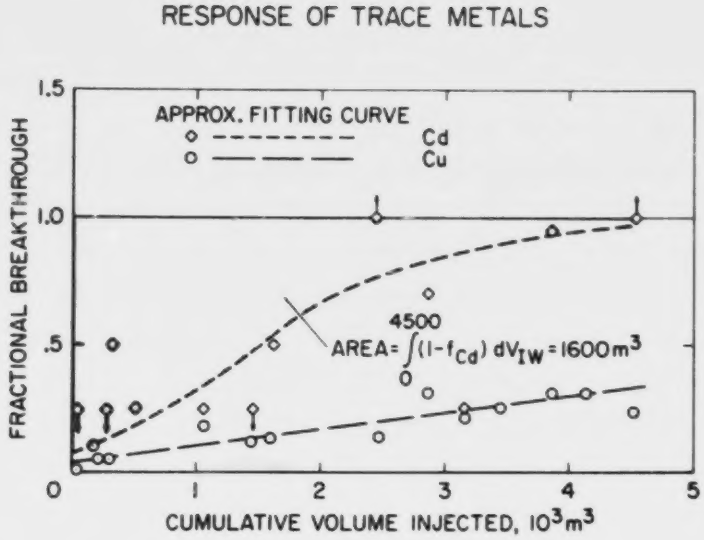


Fig. 8 Responses of Cd and Cu

Conclusions

1. Much can be learned about the behavior of trace contaminants in the groundwater environment by conducting controlled stimulus-response experiments under realistic field conditions.
2. From the response at an aquifer sampling point following a step change in concentration at the injection point, insights into water quality changes can be obtained. The processes responsible for removal can be identified tentatively. The transport rate relative to water and the effective field capacity can be estimated for compounds for which complete breakthrough is observed.

3. Evidence of degradation in the aquifer environment was seen for naphthalene and possibly styrene. Naphthalene was degraded to a steady-state concentration of 0.5×10^{-9} mol per liter following initial breakthrough.
4. Chlorinated aliphatic and aromatic compounds are retained effectively by adsorption during aquifer passage. Their concentrations initially are reduced to less than 0.1 μg per liter. However, the adsorption capacity ultimately is satured and breakthrough occurs.
5. The specific field retention capacity for chlorobenzene was estimated to be 0.032 g chlorobenzene per m^3 aquifer, at an average injected concentration of 4 μg per liter. The specific retention capacity for chloroform was a factor of ten smaller, 0.0032 g chloroform per m^3 aquifer at approximately the same injected concentration.
6. Organic micropollutants vary widely in the rate at which they are transported through an aquifer. The chlorinated aliphatic compounds, exemplified by chloroform, are transported most rapidly among the substances studied in this work. Chloroform was transported one-fifth as rapidly as the water with which it was injected. Chlorinated aromatic compounds are transported much less rapidly. Chlorobenzene moved 36 times more slowly than the injected water, for example. Dichlorobenzene and trichlorobenzene isomers are transported much more slowly.
7. Trace metals are removed in the aquifer by adsorption. Cd was transported most rapidly among the trace metals studied. Cd travelled with a velocity one-fortieth that of the injected water. The specific field retention capacity for Cd was 0.017 g Cd per m^3 aquifer.

Acknowledgments

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(1) ROBERTS, P.V., McCARTY, P.L., REINHARD, M., SCHREINER, J.
Direct Injection of Reclaimed Water into an Aquifer
J. Environ. Div. ASCE (1978) (in press)

(2) McCARTY, P.L., SCHERTENLEIB, R., NIKU, S.
Preproject Water Quality Evaluation for the Palo Alto Water Reclamation Facility
Technical Report No. 206, Civil Engineering Department, Stanford University, Stanford, CA (1976)

(3) BELLAR, T.A., LICHTENBERG, J.J.
Determination of Volatile Organics at the µg/l Level in Water by Gas Chromatography
J. AWWA 67 (1974), 634

(4) GROB, K., ZÜRCHER, F.
Stripping of Trace Organic Substances from Water
J. Chromatography 117 (1976), 285

(5) ROBERTS, P.V., McCARTY, P.L., REINHARD, M.
Direct Injection of Reclaimed Water: Attenuation of Organic Contaminant Movement
J. WPCF, submitted for publication (1978)

(6) LEVENSPIEL, O.
Chemical Reactor Engineering
Wiley, New York (1962)

(7) FRIED, J.J.
Groundwater Pollution
Elsevier Scientific Publishing Co., Amsterdam (1975)

(8) SIEVERS, R.E. et al.
Generation of Volatile Organic Compounds from Nonvolatile Precursors in Water by Treatment with Chlorine or Ozone
Water Chlorination: Environmental Impact and Health Effects, Ann Arbor Science Publ. Inc. Ann Arbor, Mich. 2 (1978), 615-624

(9) McCARTY, P.L.
Energetics of Organic Matter Degradation
Water Pollution Microbiology, Wiley Interscience, Inc., New York (1972), 5

(10) SIELICKI, M., FOCHT, D.P., MARTIN, J.P.
Microbial Transformations of Styrene and C^{14} Styrene in Soil and Enrichment Cultures
Appl. and Environm. Microbiology 35 (1978), 1, 124

(11) WAGNER, R.
Abbaubarkeit und Persistenz
Vom Wasser 40 (1973), 335

BIOLOGICAL PROCESSES FOR THE TREATMENT OF DRINKING WATER

J. Chedal

Following the lectures of this morning I should like to describe our experience with the biological elimination of ammonia.

We tested the sludge-bed clarification plant described by Dr.J.B.Goodall and found that this process has two disadvantages when applied to the raw waters used by us:

- fluctuating ammonia elimination rates
- when starting from an empty plant, a very long time until an active sludge layer is formed (about 1 month).

The use of sand particles as in the Fluorapid plant definitely makes it possible to eliminate the latter disadvantage to a certain extent. It should be added by way of explanation that our experiments were performed with water containing less than 2 ppm of ammonia.

It has also been established that the above-mentioned drawbacks can be partially eliminated by increasing the ammonia content in the water. However, we consider it ridiculous to add ammonia to the water only to remove it again. For this reason we do not plan to incorporate a process of this kind.

As regards the biological filtration, the experiments so far have shown that this plant operates much more satisfactorily and delivers constant deposition of about 80% even in winter.

The main features of the plant are:

- increased water flow (maximum velocity about 18 m/h)

- air flow
- carrier layer enriched with trace impurities of the type of Biodamine.

As is well known, the filter is of the over-damming design, in contrast to the bacteria beds in clarification plants.

In conclusion, reference may be made to the biological activity of the rarely-mentioned storage process.

Our experiments have shown that with a residence time of 2 days this process makes it possible to eliminate about 50% of the ammonia.

NITROGEN REMOVAL IN BIOLOGICAL REACTORS AT LOW TEMPERATURES

G. Halmø, K. Eimhjellen and T. Thorsen

Laboratory tests have been performed with continuous biological reactors treating sewage and organic chemicals at low temperatures. Three steps were operated in series: Activated sludge, nitrification and denitrification. Most effort was done to investigate the denitrification step and its performance.

The tests

Both activated-sludge and denitrification steps have shown better performance using psycrophilic or psycrotrophic sludge if water temperatures are low. The low-temperature bacteria have significant effectiveness right down to 0°C, optimum at about 15°C and maximum at about 20°C. Previous tests have shown that a developed low-temperature sludge has greater denitrification velocity than high-temperature (mesophilic) sludge over a greater part of the low-temperature range. It has been realized, however, that around 17°C, an irreversible change destroys the good performance of low-temperature operation.

Tests in a continuous laboratory plant, involving all three steps, have been done at 5 ± 1°C. Due to high COD reduction in the act, sludge step, methanol was added to the denitrification step to ensure enough feed for the bacteria. Between each change in operating conditions, 1-4 weeks was allowed to attain pseudo-equilibrium.

Results

Because of unpredicted destruction of the Nitrobacter-types in the nitrification step, this step only oxidized ammonia to nitrite during the later part of the tests. However, this did not influence the effectiveness of the denitrification step. Mean values from several tests are shown in Table 1.

The results show that biological N-removal is easily obtained at low temperatures. With the mentioned residence times approx. 90% of total N is removed in sewage at 5°C. The nitrification/denitrification steps remove approx. 95% of N from the act-sludge step. Denitrification alone is more than 98% effective. Previous tests indicate that about equal performance can be expected at least down to 3°C. With increasing temperature up to about 17°C, the same performance may be attained with shorter residence times.

TABLE 1 Mean values of test results for nitrogen (ppm)

Influent		After activated sludge		After nitrification		After denitrification	
NH_4^+	$NO_2^-+NO_3^-$	NH_4^+	$NO_2^-+NO_3^-$	NH_4^+	$NO_2^-+NO_3^-$	NH_4^+	$NO_2^-+NO_3^-$
43	0.6	27	2.2	2.5	25	1.5	0.4
48	0.5	34	0.6	9	32	8	0.4
Res. time →		1.5 hours		9 hours		4 hours	

NB: First line: Mainly NO_3^- produced in nitrification step;

Second line: Mainly NO_2^- produced in nitrification step.

Sedimentation of psycrophilic sludges is significantly better than corresponding mesophilic sludges. No bulking problems were observed contrary to experiences with mesophilic sludges in the same plant.

Only methanol was used as electron-donor and source of carbon. Approx. 3 mg methanol is needed for each mg of N. Microbiological investigations show that none of the dominant bacteria are obligate methylotropes.

The results show that psycrophilic/psycrotrophic sludges can be used with advantage for removing N at low temperatures, particularly below 5°C. It seems that nitrification is the most sensible step, and further investigations should be performed here.

Even though these experiments were done with sewage and chemicals, the results in general should be useful to drinking water treatment.

MICROBIOLOGICAL STUDIES ON ACTIVATED CARBON FILTRATION

P. Werner, M.Klotz and R. Schweisfurth

1. Introduction

The results relate to the processing of Rhine water into drinking water by means of activated carbon.

In regards to the method, the determination of the microorganism count in the water poses no real problems if suitable nutrient media, incubation temperature, and incubation time are used after appropriate preliminary treatment. Determination of the colony counts in water according to the recommendations of the Deutsche Einheitsverfahren is unsatisfactory, since this method only reflects a very small and non-representative part of the microflora. The reported colony counts were obtained by a special method and are substantially higher than ones obtained according to the Deutsche Einheitsverfahren. Therefore, in the light of these values, no statements on the hygienic and bacteriological state of the water can be made in accordance with the current Drinking Water Decree (Trinkwasserverordnung)[1].

2. Quantitative determination of microorganism populations

When activated carbon is used in the treatment of drinking water a bacterial population in the filtrate always occurs. The colony counts in the characteristic treatment stages are shown in Fig. 1.

As a rule colony counts of $2 \cdot 10^5$/ml are found in the raw water. By means of the preliminary chemical treatment of the water the colony counts can be reduced to about 10^3/ml before the input to the activated carbon filter. If this is followed by a high-dose chlorination, nearly all the bacteria are destroyed. In the activated carbon filter an increase of the bacteria to values of about $7 \cdot 10^4$/ml again occurs. The activated carbon filter outflow is normally hygienically and bacteriologically unimpeachable in accordance with the current Drinking Water Decree.

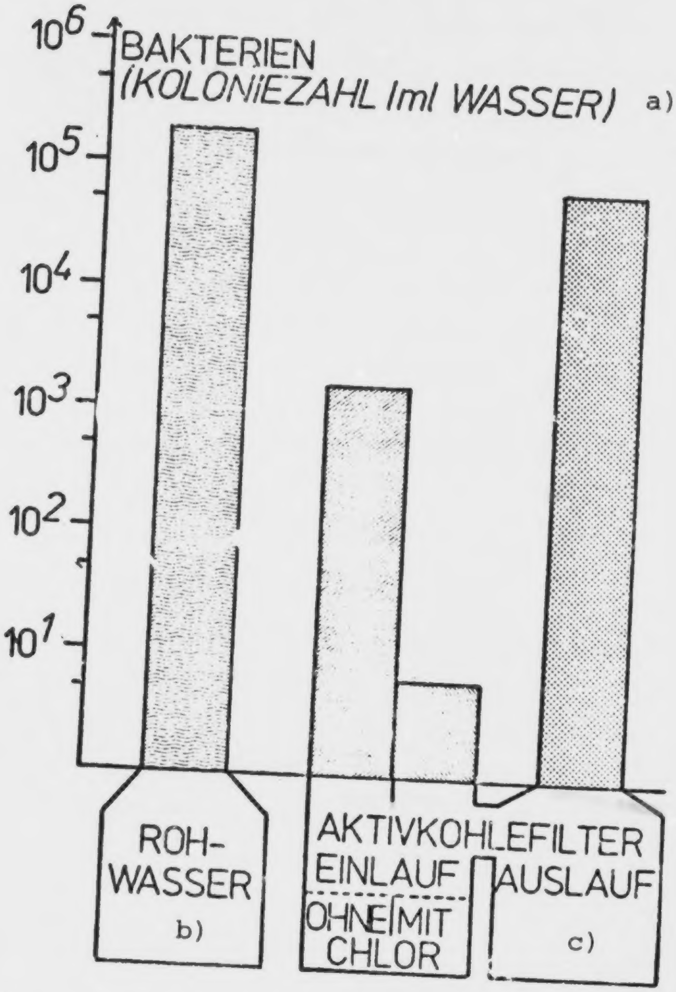


Fig. 1 Colony counts on SPC Agar at characteristic treatment stages in a Rhine water treatment plant

Key: a) = Bacteria (colony count/ml water)
b) = Raw water
c) = Activated carbon filter
inlet outlet
with/without chlorine

Approximately a thousand times more bacteria per unit volume can be found on the carbon than in the water by colony count determinations.

Since culture methods can never include all the live bacteria, the living cell count is determined by enzymatic methods. The total cell count (all living and dead bacteria) was determined microscopically after enrichment on membrane filters [2].

The colony count determination reflects up to 20% of all living bacteria and up to 5% of the total cell count, i.e. one including both living and dead bacteria.

3. Qualitative determination of microorganism populations

3.1. Comparison of the populations in raw water and in the carbon filter

A comparison of populations with the methods of numerical taxonomy should make it clear whether the bacterial flora changes in the course of the water treatment, while the colony count remains practically unchanged. The morphological and biochemical properties of the bacterial strains were determined and later compared with the aid of a computer.

It was found that:

- the adaptability of the bacteria in the activated carbon filter is lower than that of the bacteria in the raw water,
- there are proportionally more bacteria of the Pseudomonas genus in the activated carbon filter than in the raw water,
- the populations differ clearly in respect of the utilization of substrates, in particular harmful substances.

A special microorganism population thus develops in the activated carbon filter, which is different from that of the raw water, although both populations have almost the same colony counts.

3.2. The species composition of a microorganism population

3.2.1. Bacteria

A total of 26 species were isolated, belonging to 11 genera (Table 1). The majority of the bacteria belonged to the genus Pseudomonas. From the point of view of species, the genera Bacillus and Azomonas were also well represented. The bacteria found are not pathogenic and are normally present in water.

Table 1 Bacterial species in the water of an activated carbon filter

Pseudomonas alcaligenes
Pseudomonas cepacia
Pseudomonas facilis
Pseudomonas flourescens
Pseudomonas lemoignei
Pseudomonas mendocina
Pseudomonas ruhlandii
Pseudomonas stutzeri
Pseudomonas spec.
Gluconobacter oxidans
Azomonas agilis
Azomonas insignis
Azomonas macrocytogenes
Chromobacterium violaceum
Neisseria sicca
Acinetobacter calcoaceticum
Micrococcus luteus
Staphylococcus saprophyticus
Bacillus cereus
Bacillus circulans
Bacillus licheniformis
Bacillus megaterium
Bacillus pumulis
Bacillus thuringensis
Corynebacterium spec.
Micromonospora spec.

3.2.2. Fungi

Moulds and yeasts are found seldom and irregularly in the activated carbon filtrate. They therefore play a subordinate role in the treatment of water.

Table 2 gives a summary of the moulds and yeasts which are found in the water of the activated carbon filters. The fungi present are non-pathogenic.

Table 2 Fungal species in the water of an activated carbon filter

Phialophora hoffmannii
Phialophora mutabilis
Taphrina spec.

Rhodotorula minuta var. texensis
Cryptococcus uniguttulatus
Candida guilliermondii var. guilliermondii
Hansenula anomala var. anomala

3.3. Bacterial capacity

Activated carbon adsorbs organic substances that can serve as a substrate for the bacteria, but it also adsorbs bacteria, this adsorption following Freundlich's isotherm (Fig. 2).

Because of the large difference in sizes, the bacteria and the substrate are separated spatially by the pore structure of the activated carbon during the adsorption. This has a secondarily adverse effect on the bacterial metabolism. In the absence of activated carbon the bacteria and the substrate are distributed uniformly or enriched at the same points.

Fig. 3 shows the metabolic activity of the bacteria as a function of time. The oxygen consumption serves as a measure of metabolic activity. Without activated carbon the degradation of the substrate proceeds essentially more rapidly.

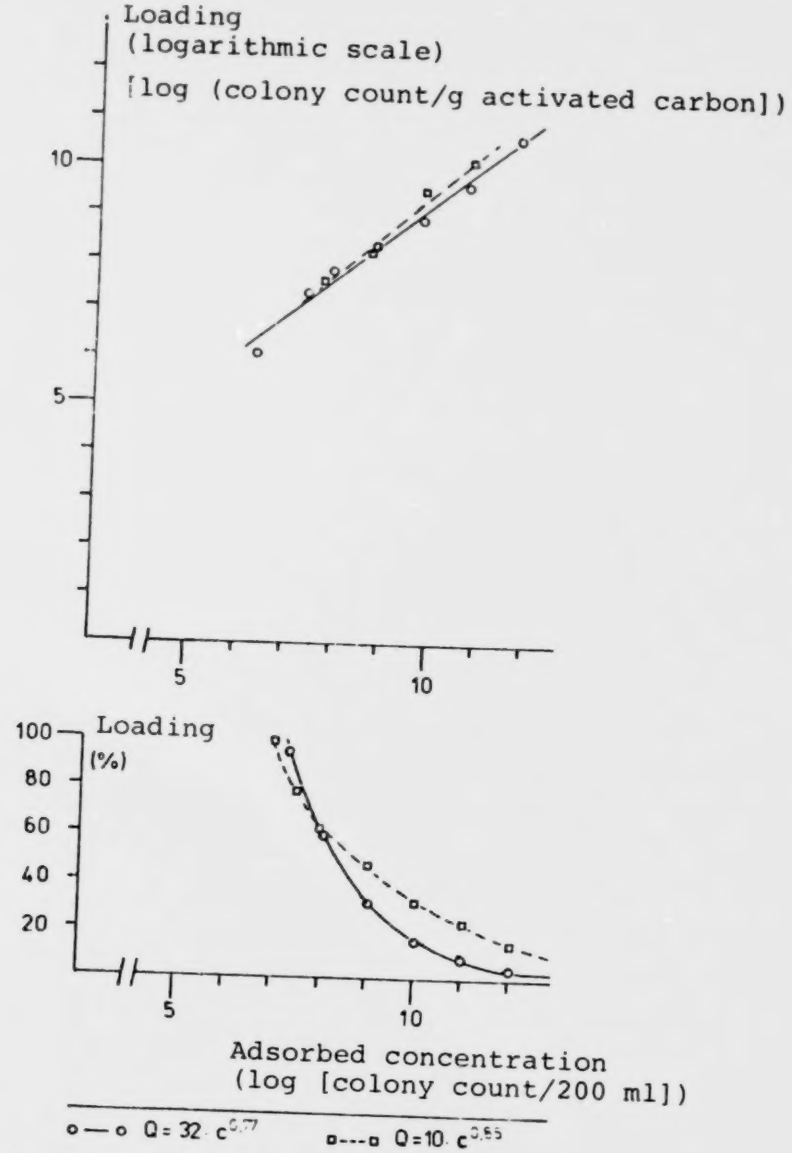


Fig. 2 Studies on the adsorption of bacteria on activated carbon. Isotherms

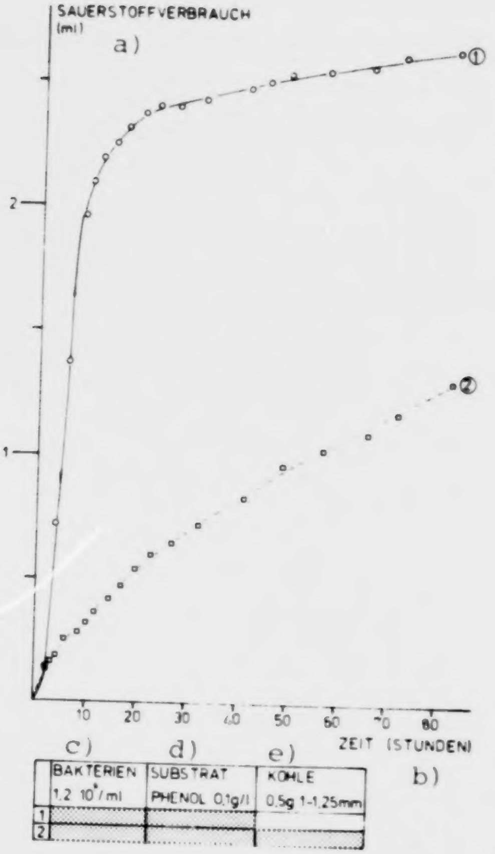
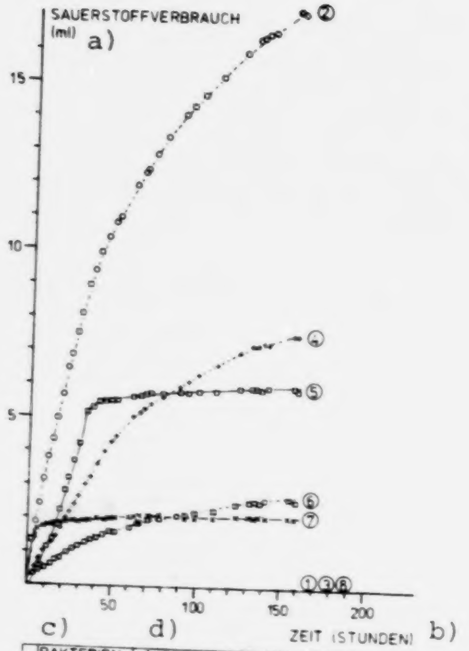


Fig. 3 Studies on the effect of activated carbon on the metabolic activity of bacteria
Utilization of phenol

Key: a) = Oxygen consumption (ml)
b) = Time (h)
c) = Bacteria
d) = Substrate
Phenol, 0.1 g/l
e) = Carbon,
0.5 g, 1-1.25 mm

Activated carbon also has a beneficial effect on the metabolism of the bacteria. It enriches organic substances and increases their residence time in the filter; a buffering of the system also occurs when toxic substances are present.

Fig. 4 represents the outcome of degradation experiments with four different concentrations of phenol.



c) d)

	BAKTERIEN 3,5 10⁹ /ml	SUBSTRAT PHENOL 2,5 g/l	1 g/l	0,3 g/l	0,1 g/l	KOHLE 0,5g 1 - 1,25 mm
1	▨	▨				
2	▨	▨				▨
3	▨		▨			
4	▨		▨			▨
5	▨			▨		
6	▨			▨		▨
7	▨				▨	
8	▨				▨	▨

e)

Fig. 4 Studies on the effect of activated carbon on the metabolic activity of bacteria
Utilization of various phenol concentrations.

Key: a) = Oxygen consumption (ml)
b) = Time (h)
c) = Bacteria
d) = Substrate
Phenol, 0.1 g/l
e) = Carbon, 0.5 g, 1-1.25 mm

At high phenol concentrations no degradation was found in the absence of activated carbon, due to the toxicity of this substance. The following was found when activated carbon was present: the carbon adsorbs the phenol, renders it "harmless", and releases it continuously in the manner of a slow-flowing carbon source in non-toxic concentrations.

3.3.1. Contribution of the bacteria to the water treatment

The following values apply to the drinking water treatment of Rhine water with high chlorination before the activated carbon filtration. At the time of the studies the activated carbon filter had an efficiency of about 80%. The bacteria participated as follows in this treatment:

- reduction of the amount of dissolved organic substances: 5%,
- reduction of the amount of readily degradable organic substances (BOD_2): about 70%,
- reduction of the amount of difficultly degradable organic substances (BOD_{20}): about 17%
- oxygen consumption: about 60%,
- carbon dioxide production: about 60%.

It should be noted that during the subsequent inevitable decrease in the adsorption capacity of the activated carbon the bacterial fraction increases strongly in activity. The already low degradability of the organic substances in this water is additionally reduced by the high chlorination. The high degree of the decrease of readily degradable organic substances is significant as regards the repopulation with bacteria. These substances, causing the repopulation, are partly removed by the biologically active activated carbon filter and thus the tendency towards bacterial population of water in the supply network is reduced.

In addition, it must be mentioned that the bacterial activity effects a continuous partial regeneration of the carbon and so prolongs its running time.

4. Discussion and outlook

The occurrence of microorganisms and their proliferation in the activated carbon filter was felt to be undesirable in the past - and sometimes still today - without any exact knowledge of the microbiological relationships and their significance.

Accordingly, processes for disinfection of the activated carbon filters were developed, which proved to be of no use on a large industrial scale.

Bacteria on the activated carbon should not be combatted. On the contrary, their activity should be promoted, i.e. their contribution, manifested ultimately in the conversion and mineralization of organic substances, should be optimized by suitable measures. An example of this is offered by experiments in which high chlorination - which among its other adverse effects impairs the degradability of the water constituents - is replaced e.g. by ozonization to keep the readily degradable compounds in the water.

(1) KLOTZ, M., WERNER, P., SCHWEISFURTH, R.
Mikrobiologische Untersuchungen der Aktivkohlefiltration zur Trinkwasseraufbereitung
Forschung und Entwicklung in der Wasserwerkspraxis
Wissenschaftl. Berichte über Untersuchungen und Planungen der Stadtwerke Wiesbaden AG 3 (1976), 75-82

(2) KLOTZ, M., WERNER, P., SCHWEISFURTH, R.
Untersuchungen zur Mikrobiologie der Aktivkohlefilter
7. Vortragsreihe mit Erfahrungsaustausch über spez. Fragen der Wassertechnologie
Veröffentl. des Bereichs und des Lehrstuhls f. Wasserchemie der Universität Karlsruhe (1975) 9, 270-282; English translation: EPA 600/9-76-030 Dec. (1976)

PROCESSES DURING BIOLOGICAL OXIDATION IN FILTERS

D. van der Kooij

Introduction

Biological processes, which result in the oxidation of organic and some inorganic compounds as well as in the removal of bacteria of hygienic significance from water have always been important in drinking water preparation. However, the increased pollution of water resources by pathogenic micro-organisms and non-biodegradable compounds forced the waterworks to extend their water treatment systems by addition of physicochemical processes including oxidation, adsorption and disinfection. These techniques may have direct effects on biological and physicochemical processes, therefore selection and sequence of both biological and physicochemical processes are of major importance to obtain optimal treatment efficiency.

Some recently introduced combinations of physiochemical and biological processes are: ozonation followed by filtration and the use of granular activated carbon (GAC) filters in which adsorption and biological oxidation occur next to each other. This paper focusses on some interactions between adsorption and biological activity in GAC-filters applied to prepare drinking water.

GAC-filtration proved to be very useful for the removal of dissolved toxic or taste and odour affecting organic substances originating from domestic and industrial water pollution. However, in GAC-filtrates frequently increased colony counts have been observed. (1,2,3,4,5). This increase of colony counts is in contrast with the reduction of bacterial numbers as usually observed in slow sand filters. Today it seems widely accepted that the observed growth of microorganisms in GAC-columns is enhanced by substrate enrichment in the filter bed resulting from the adsorption of organic compounds by the carbon (6,7,8,5,9, 10,11).

Moreover, some investigators concluded that an increased contact-time between organisms and substrate (adsorbed) is allowing the organisms to adapt to the less readily biodegradable organic substances. The consumption of adsorbed compounds from the carbon has been called "biological regeneration" of the carbon (12).

The application of GAC-filters in drinking water preparation in the Netherlands made it necessary to evaluate the microbiological phenomena occurring in these filters. Results of some experiments performed earlier by the author (13) revealed that die-off rates of some types of micro-organisms on GAC and granular-non-activated carbon from filters supplied with river water during one year did not differ. These results suggested that the micro-organisms were unable to utilize organic substances adsorbed on AC.

Experiments

The influence of different filter materials on the presence of micro-organisms in filter beds and filtrates was investigated using small experimental filter-columns containing GAC (Norit ROW 0.85), a non-activated carbon (GNAC) with granules of similar dimensions and sand (diameter 0.8-1.0 mm). These filter-columns (diameter 6 cm) were supplied with tap water (DOC:3 ppm, water temperature 14-18°C) without chlorine. The flow rate was 3.5 m/h and the apparent contact time was 3 minutes. During a one-year period, filter materials, filtrates and the influent were sampled and colony counts (c.f.u./ml) were estimated. For this purpose the surface spread technique on 8-fold diluted Lab-Lemco broth (Oxord CM 15.) agar plates was used. The samples of filter materials were treated ultrasonically for 3 minutes in the dilution water to detach micro-organisms. The plates were incubated at 25°C for 10 days.

Moreover, the removal of organic substances was measured by ultra-violet light absorbance at 275 nm in 5 cm cuvettes.

Results and discussion

The colonization of the filter materials and the colony counts of the tap water and the filtrates are presented in Figure 1. Maximum colony counts on the filter materials and in the filtrates were reached after a filtration period of 20 to 30 days. The ultraviolet absorbences revealed that both the GNAC filter and the Sand filter had an immediate total breakthrough of UV-absorbing compounds. The GAC-filter reached a breakthrough level of 80 % after 30 days. After 50 days only 10 % of the UV-absorbing compounds were removed by the AC-filter.

A comparison of the colony counts observed on the filter materials is presented in Figure 2. This figure reveals that the colony counts of GAC were usually larger than those of GNAC and Sand and reached

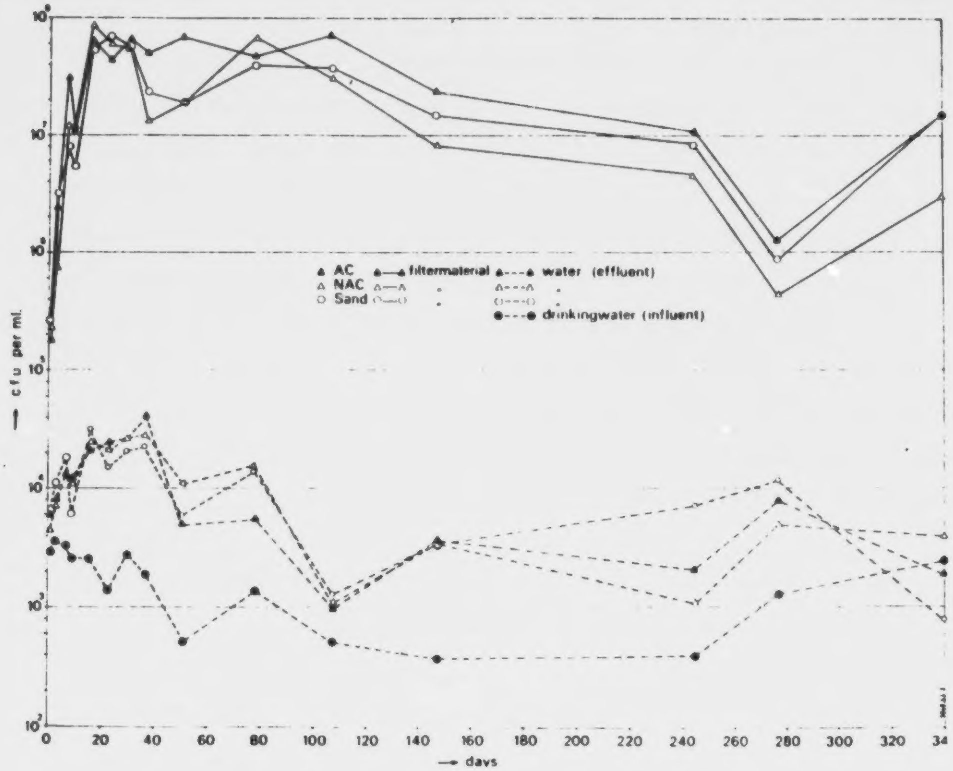


Fig. 1 Colony counts of the influent, the filter materials and filtrates during a period of 340 days

a maximum level of about $7x10^7$ c.f.u./ml. The colony counts of GNAC and sand were similar to each other. The colony counts of the filtrates did not differ from each other (cf. Figure 3).

From the observed similarities in microbial behaviour in the presence of the three different filter materials it is concluded that adsorption of organic compounds by the activated carbon is not the cause of the high colony counts as usually observed in GAC-filters. This conclusion is supported by the observation that the majority of micro-organisms isolated from GAC was only able to grow on simple non-adsorbing compounds like acetate, pyruvate and lactate, whereas adsorbing substances like aromatic compounds were not utilized.

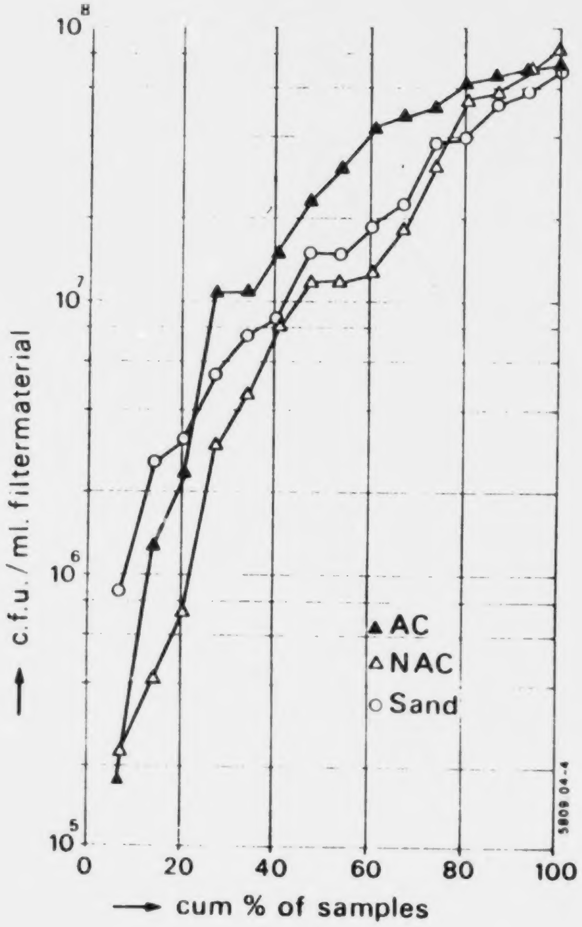


Fig. 2 Comparison of the colony counts of the filter materials GAC, GNAC and sand

Observations on sand samples from the effluent side of the slow sand filters of the Hague (flow rate : 0.3 m/hr) revealed that the bacterial content of this sand was about 2-3x10^4 c.f.u. per ml, whereas colony counts in the filtrate usually were below 100 c.f.u. per ml. Similar observations were reported by Schmidt (14). Comparison of these colony counts with those observed in the experiment (cf. Figures 2 and 3) suggested that a relationship may exist between the flow rate and the number of micro-

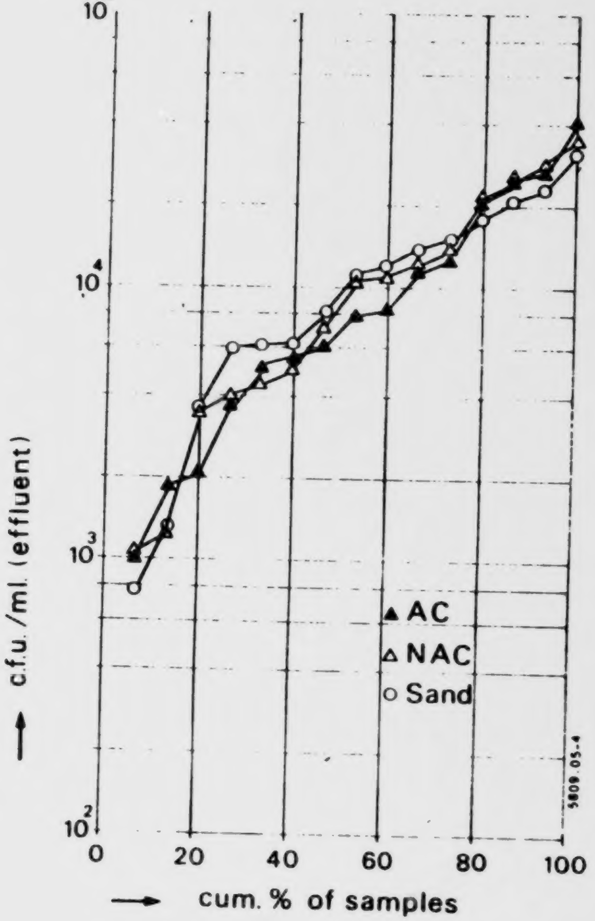


Fig. 3 Comparison of the colony counts of the filtrates from GAC, GNAC and sand

organisms on a filter material and in the filtrate, respectively. Therefore colony counts of GAC (Norit PKST) present on the slow sand filters of the Hague were estimated in samples taken from eight of these filters. The results are presented in Figure 4. Comparison of Figure 2 with Figure 4 shows that the colony counts of GAC from the slow sand filters were one to two orders of magnitude lower than those observed in the experimental GAC-filter supplied with tap water. These observations confirmed that the flow rate of the water through a filter bed is strongly affecting the colony counts of the filter materials.

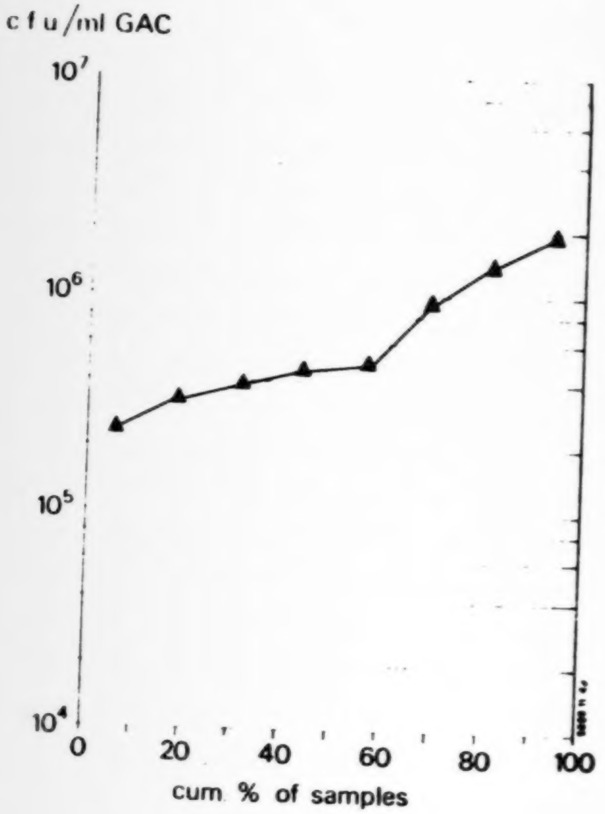


Fig. 4 The colony counts of GAC present on the slow sand filters of The Hague

The results presented in Figure 2 revealed that the colony counts of GAC were usually larger than those of GNAC and Sand although the colony counts in the filtrates did not differ. This phenomenon is probably due to the relatively large surface area per unit volume of the GAC, on which micro-organisms utilizing substrates from the passing water can attach. For this reason GAC may be a favourable material for biological filtration processes.

Effect of micro-organisms on adsorption

In the previous part of this paper it is shown that colony counts on GAC, in filter beds may reach a maximum level of about 7×10^7 c.f.u. per ml GAC (i.e. 2.10^8 c.f.u. /gram GAC). Large numbers of micro-organisms on GAC in filters were also observed by Klotz et al. (3). These large numbers of micro-organisms on the GAC might hinder the transport of organic compounds to the adsorbing surface of the carbon. Some laboratory experiments were conducted to investigate the influence of bacterial cell attached on GAC on the adsorption of some compounds. In these experiments, adsorption isotherms and adsorption rates of 4-nitrophenol and 4-hydroxybenzoate on GAC (Norit ROW 0.8 Supra) were estimated in the presence and in the absence of a large number of bacteria on the carbon. The used bacteria were a Pseudomonas fluorescens strain and a Pseudomonas alcaligenes strain. The fluorescent pseudomonad could grow on 4-hydroxybenzoate but did not utilize 4-nitrophenol, whereas P. alcaligenes could not use either of these compounds. Portions of 0.1 gram GAC were sterilized in bottles containing 200 ml demineralized water with KH_2PO_4 2.7 mg/l; $K_2HPO_4.3H_2O$ 5.3. mg/l and $Na_2HPO_4.12H_2O$ 8.0 mg/l. Final pH after sterilization: 7.3. In order to cultivate bacteria on the carbon ammonium-acetate was added to the sterilized bottles from a separately sterilized solution in a final concentration of 10 mg acetate-carbon per liter. Further, the bottles were inocculated with either the fluorescent pseudomonad or the P.alcaligenes isolate and incubated for 3 days at 25^o in a rotary shaker (120 rev/min.). The bacteria developed to the maximum level of 4×10^7 c.f.u. per ml of medium and the GAC contained about 2.10^8 c.f.u. per ml (6×10^8/gr) of carbon. In these conditions 4-nitrophenol was added to the bottles with P.fluorescens and 4-hydroxybenzoate was added to the bottles with P.alcaligenes from sterilized solutions in final concentrations of 100 mg/l; 50 mg/l; 25 mg/l and 10 mg/l. These compounds were also added to bottles containing sterilized GAC without bacteria. The bottles were replaced in the rotary incubator at 25°C and the concentrations of either 4-hydroxybenzoate or 4-nitrophenol were measured by UV-absorbance (at 245 and 269 nm, respectively) in membrane filtered samples of 5 ml after 24,48 and 144 hours of incubation. UV-absorbances were measured every hour during the first eight hours after addition in bottles with an initial adsorbate concentration of 100 mg/l. All experiments were performed in duplicate.

Results and discussion

With both compounds, the adsorption-equilibrium was reached within 48-144 hours. The adsorption-isotherms of 4-nitrophenol and 4-hydroxybenzoate on the carbon in the presence and in the abscence of bacteria were calculated from measured concentrations and are presented in Figure 5. The disappearance of the adsorbates from the solution initially containing 100 mg of adsorbate per liter is shown in Figures 6 and 7. Figures 5, 6 and 7 show that 4-nitrophenol is better adsorbed than 4-hydroxybenzoate. The results presented in Figure 5 reveal that the adsorption isotherms were not affected by the described presence of the bacteria. Moreover, the adsorption of the adsorbates in the 100 ppm-bottles was not affected by the presence of bacteria on the carbon. The adsorption rate of 4-hydroxybenzoate in

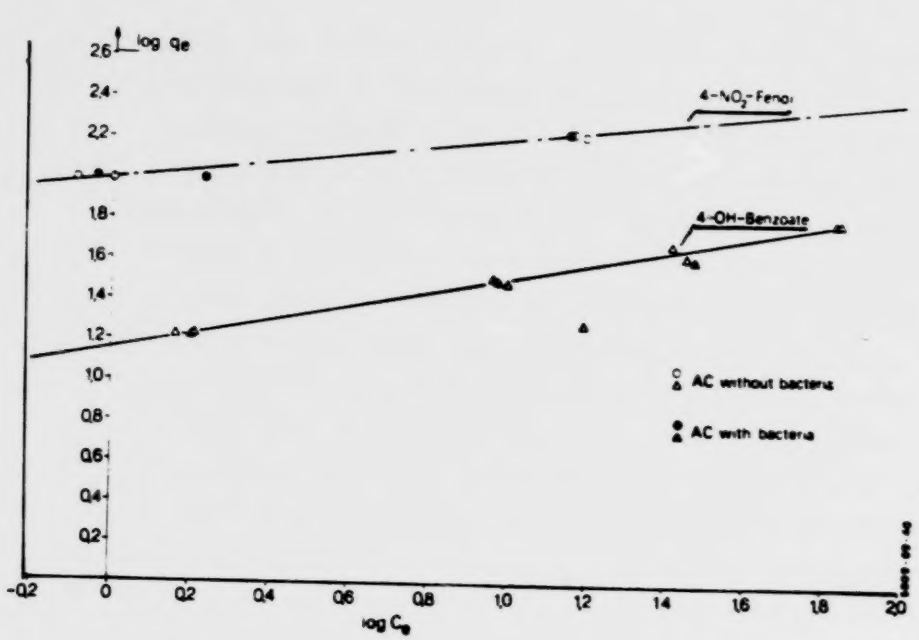


Fig. 5 The adsorption isotherms (144 hours) of 4-nitrophenol and 4-hydroxybenzoate on GAC (Norit ROW 0.8 Supra) in the presence and in the absence of bacteria on the carbon

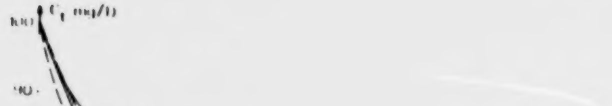


Fig. 6

The disappearance of 4-nitrophenol and 4-hydroxybenzoate from a solution as a result of adsorption on GAC with and without bacteria

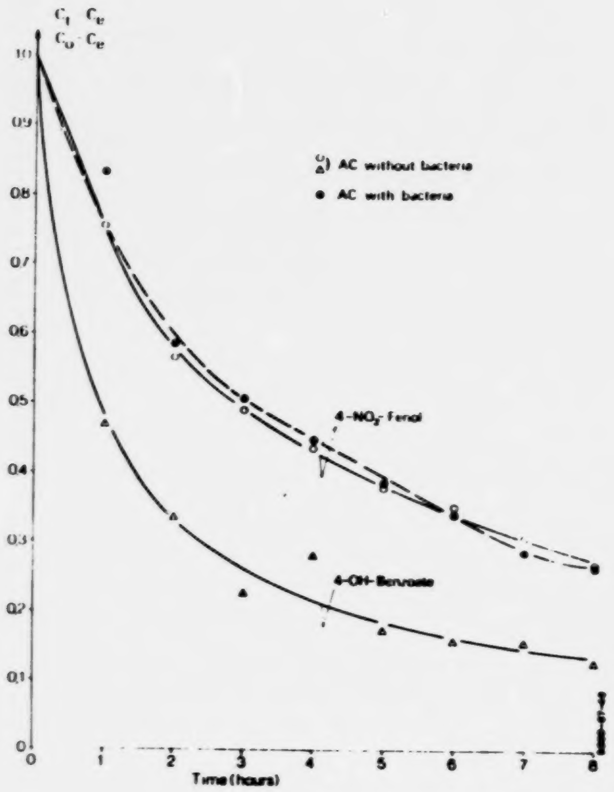


Fig. 7

the presence of bacteria could not be calculated because both bottles became infected by adsorbate-consuming micro-organisms. This compound is, in contrast to 4-nitrophenol, easily biodegradable.

The experiments described in this paper showed that the number of micro-organisms on a filter material depends on the flow rate of the water through the filter bed. This phenomenon is probably due to limitation of substrate transport to the micro-organisms. Moreover, it is shown that adsorption of compounds was not inhibited by the presence of a large number of bacteria on the carbon. GAC in filter beds sampled by the author always had lower colony counts than the level applied in the experiments described in this paper. Therefore it is concluded that in most GAC-filters used to prepare drinking water, hinderance to the adsorption of organic compounds by micro-organisms is very unlikely. However, it still may occur when the water is containing relatively large amounts of biodegradable compounds in which situations extremely large numbers of micro-organisms develop on the carbon. Moreover, adsorption may be affected by the pollution of GAC by colloidal and suspended matter. These effects were not investigated.

(1) FORD, D.B.
The use of granular carbon filtration for taste and odour control
Proc. Wat. Res. Ass. Conf. Reading (1973), 263-278

(2) KNOPPERT, P.L., ROOK, J.J.
Treatment of river Rhine water with activated carbon
Proc. Wat. Res. Ass. Conf. Reading (1973), 109-125

(3) KLOTZ, M., WERNER, P., SCHWEISFURTH, R.
Investigations concerning the microbiology of activated carbon filters
Trans. Rep. Special Problems Water Technol. EPA-600 19-76-030 (1976), 312-330

(4) MELBOURNE, J.D., MILLER, D.G.
The treatment of river Trent water using granular activated carbon beds
Proc. Wat. Res. Ass. Conf. Reading (1973), 73-108

(5) WALLIS, G., STAGG, C.H., MELNICK, J.L.
The hazards of incorporating charcoal filters into domestic water systems
Water Research 8 (1974), 111-113

(6) WEBER, W.J., FRIEDMAN, L.D., BLOOM, R.
Biologically extended physicochemical treatment
Adv. Wat. Poll. Res., Proc. 6th Internat. Conf. Jerusalem (1972), 641-656

(7) KÖLLE, W., SONTHEIMER, H.
Experience with activated carbon in West Germany
Proc. Wat. Res. Ass. Conf. Reading (1973), 347-367

(8) LOVE, O.T., ROBECK, G.G., SYMONS, J.M., BUELOW, R.W.
Proc. Wat. Res. Ass. Conf. Reading (1973), 279-312

(9) EBERHARDT, M.
Untersuchungen zur optimalen Kombination von Adsorption, Filtration und biologischer Reinigung
Publication Wasserchem., Engler-Bunte-Inst., Univ. Karlsruhe 5 (1971), 358-279

(10) GUIRGUIS, W., COOPER, T., HARRIS, J., UNGAR, A.
Improved performance of activated carbon by preozonation
J. Wat. Poll. Contr. Fed. 50 (1978), 308-320

(11) SYMONS, J.M.
Interim treatment guide for controlling organic contaminants in drinking water using granular activated carbon
US EPA, Cincinnati (1978)

(12) EBERHARDT, M.
Experience with the use of biologically effective activated carbon
Trans. Rep. Special Problems Wat. Technol.
EPA-600/9-76-030 (1976), 331-347

(13) Van der KOOIJ, D.
Some investigations into the presence and behaviour of bacteria in activated carbon filters
Transl. Rep. Special Problems Wat. Technol. EPA-600/9-76-030 (1976), 348-354

(14) SCHMIDT, K.
Die Abbauleistungen der Bakterienflora bei der Langsamsandfiltration und ihre Beeinflussung durch die Rohwasserqualität und andere Umwelteinflüsse
Publication Hydrol. Forsch. Dortmund, Dissertationsschr. (1963), 5

PROCESS ENGINEERING ASPECTS IN THE COMBINATION OF CHEMICAL AND BIOLOGICAL OXIDATION

H. Sontheimer

Biological processes for removing dissolved organic substances from water can only be applied successfully in the treatment of drinking water if the substances to be removed are biologically degradable in the time set by the selected process and under the prevailing ecological conditions. Furthermore, the water must not contain materials that are harmful to microorganisms. As a result of these restrictions, but sometimes also for purely technical reasons, other purification measures must first be introduced before the biological treatment process can be run reliably and effectively.

Among the most important of these are the processes that allow a far-reaching removal of solids and colloids, i.e. flocculation, sedimentation, and filtration. These are performed mainly to relieve the loading on the filter surfaces in the biological filters and to prevent them from blocking up. Measures of this kind are especially necessary where the access to the infiltration surfaces for the purposes of cleaning is limited. For this reason particularly high demands are made in the case of underground seepage galleries and absorption wells. A preliminary treatment is here almost invariably necessary.

If a flocculating agent is added in such treatment processes preceding the biological purification, in many waters an additional removal of the dissolved organic substances takes place, so genuinely relieving the biological stage. Fig. 1 shows, in the light of the results obtained at Gelsenwasser AG, that a preliminary purification of this kind also has a beneficial effect on the water quality after the soil passage.

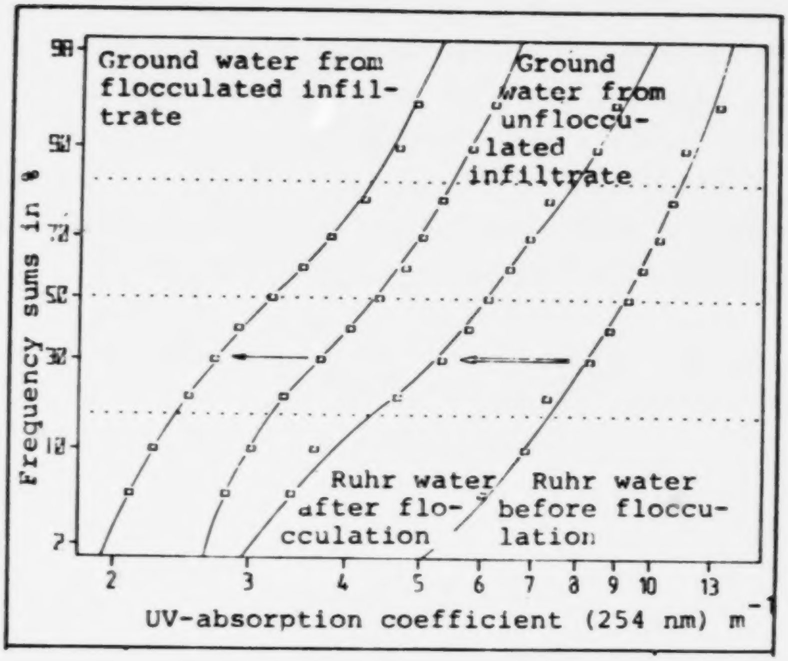


Fig. 1 Improvement of the quality of ground water by infiltration of flocculated water at the Witten waterworks

This figure shows the frequency distributions for organic substances determined by UV extinction before and after flocculation. The results indicate that the decrease in the organic loading caused by precipitation with the flocculating agent still persists after the soil passage.

A very similar result as regards the final outcome can be achieved with a process of a very different kind, namely with the aid of chemical oxidation upstream of the biological purification stage. Although chemical oxidation on its own is generally insufficient to reduce the total concentration of dissolved organic carbon, but only the chemical oxygen demand, this effect shows, just like the clear reduction of the UV extinction when ozone is used, that when a chemical pre-oxidation of this kind is performed a conversion of the organic water constituents takes place. In addition to the reduction of the mean molecular weight already mentioned in other papers, particularly with ozonization, this pre-oxidation also causes a rise in polarity by increasing the proportion of the carboxyl groups and thereby a simultaneous partial conversion of biologically resistant organic substances into biologically degradable ones (1,2).

An example of this effect, which is representative for many similar observations, is shown in Fig. 2.

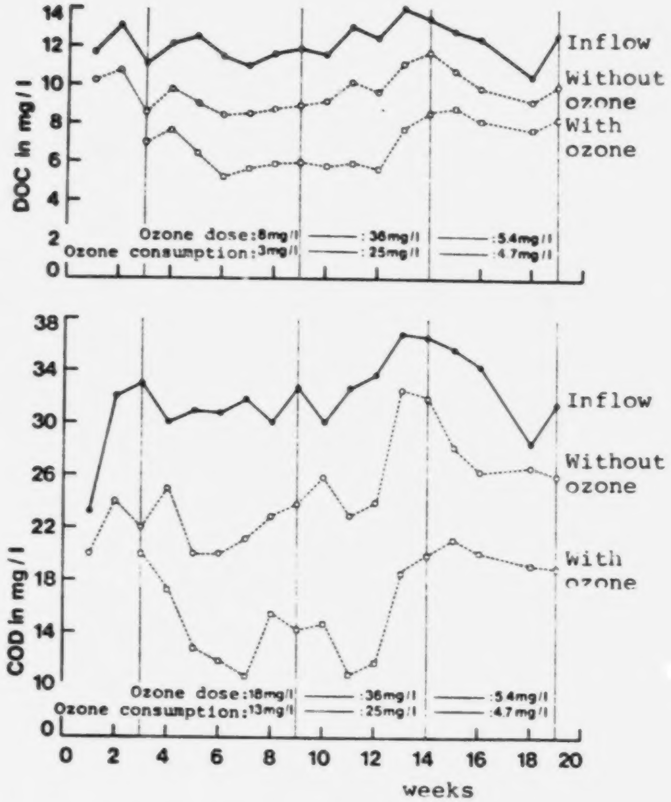


Fig. 2 Influence of ozonization on the change in the DOC and COD in the slow filtration of a biologically pre-purified waste-water

Here are shown the results for the further purification of a Berlin waste water that has already been very effectively biologically purified (3). It can be seen that by the treatment with ozone in combination with biological oxidation in a sand filter a clear improvement in both the DOC and the COD may be attained.

In connection with the theme of the present paper there is a finding - also shown in Fig. 2 - that is particularly important. It is that the favourable effects of preliminary ozonization can be easily detected when only 5.4 mg/l of ozone has been used. No further detectable improvements are obtained by the use of higher doses. All the experience gained so far with very different waters shows that on the whole only about 0.5 g/g DOC is necessary for such preliminary oxidizing treatment with ozone, and that the ozone requirement never exceeds 1 g/g DOC. This applies to crude water of normal composition, such as is used to obtain drinking water.

When using slow filters or soil infiltration large surfaces or suitable underground conditions are normally necessary. Since these are not always available, much time has been spent on the possibility of performing biological purifications in filters as well, and in this content biologically and adsorptively working activated carbon filters have aquired particular significance in recent years. The biological processes that occur here have long been observed but, owing to the high bacterial counts found in many cases, they have often been regarded as merely disadvantageous.

The increased interest in chemical and biological oxidation with the use of activated carbon filters in recent years is partly due to the results of studies carried out initially at the municipal works in Bremen (4,5) and of subsequent studies both at an experimental plant and at a main plant in Mülheim (6). Details of the experiments and experience in Mülheim will be given in the next lecture. Right now, however, using fairly simple arguments and model considerations, we shall attempt to arrive at some conclusions about what can be achieved with a process of this kind, about its limitations, and how the observations made at various plants can be explained.

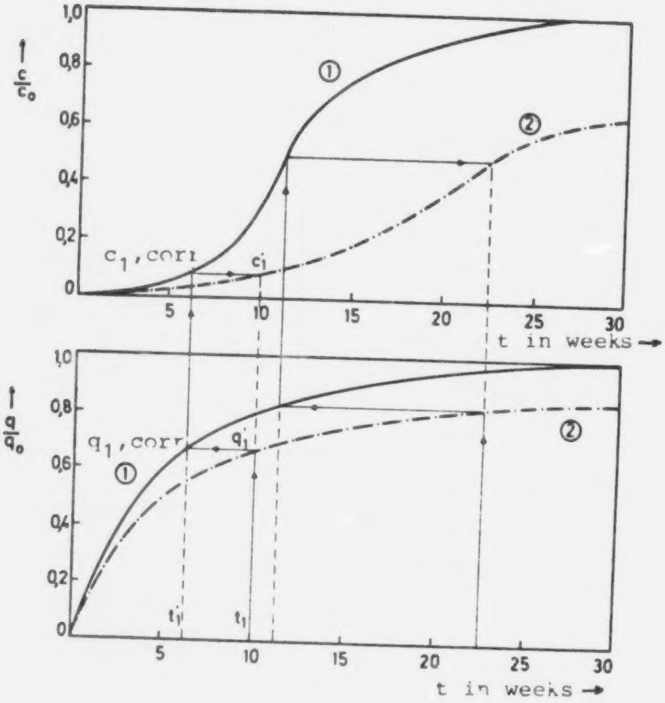


Fig. 3 Filter breakthrough curves with (-·-·-) and without (———) biological reactivation

We start out from the premise that for a given water and a given activated carbon filter the loading will increase steadily with time in the case of pure adsorption, as can be seen from curve 1 in the lower half of the figure. If the organic substances are removed by adsorption processes alone, then, depending on the nature of the organic materials and on the quality of the carbon, to each given loading in the filter there will correspond a certain outflow concentration or a certain filter efficiency. The higher the loading, the greater is the outflow concentration, as can be seen on the example of curve 1 in the top half of the figure.

It has been shown repeatedly that biological processes can lead to a reduction of the loading, since by means of these the adsorbed materials are then oxidized to CO_2 and H_2O. If a certain biological activity is assumed in the filter, we obtain curve 2 for the time variation of the loading in curve 1, i.e. with a biologically operating filter the loading increases more slowly than with pure activated carbon.

On the strongly simplifying assumption that the relationship between the loading and the filter efficiency remains constant, the breakthrough curve 2 can be easily obtained from the two loading curves and the filter activity curve 1, as is shown here as an example, if an additional biological regeneration of the activated carbon takes place. The better this regeneration, the longer is the service life of the filter until a certain residual concentration has been reached. In the simple example of a filter with a short residence time shown in Fig. 3 the running time is prolonged by about 50%. In practice the corresponding values are usually considerably higher. A prolongation of the running time by a factor of 3 - 5 is frequently observed, this factor being decisively dependent on the residence time of the water in the filter and on the proportion of biologically degradable substances.

As shown in the next figure, it is also of significance for prolonging the running time whether an appreciable part of the adsorbed substances is biologically degradable. In the case of a high proportion of resistant materials these concentrate on the carbon in the course of time. The biological

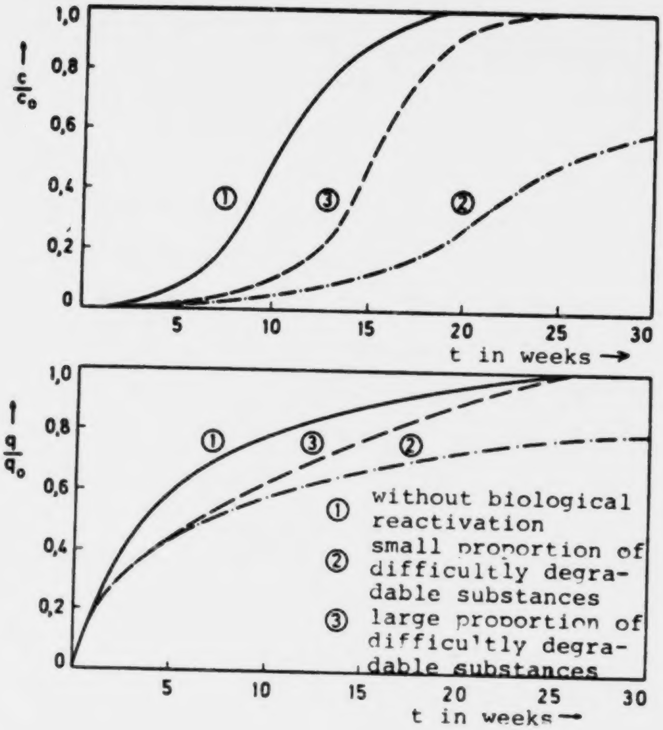


Fig. 4 Breakthrough and loading courses for biological activated carbon reactivation

activity must therefore gradually decrease, since smaller amounts of degradable materials are present on the carbon, giving rise to a considerably earlier breakthrough - represented by curve 3 - in place of the improved breakthrough curve 2.

Among other reasons, this loading with biologically resistant substances becomes evident from the fact that the oxygen consumption for the biological oxidation decreases with increasing loading.

This is shown in the following figure, based on results obtained by Engels at the Düsseldorf municipal works.

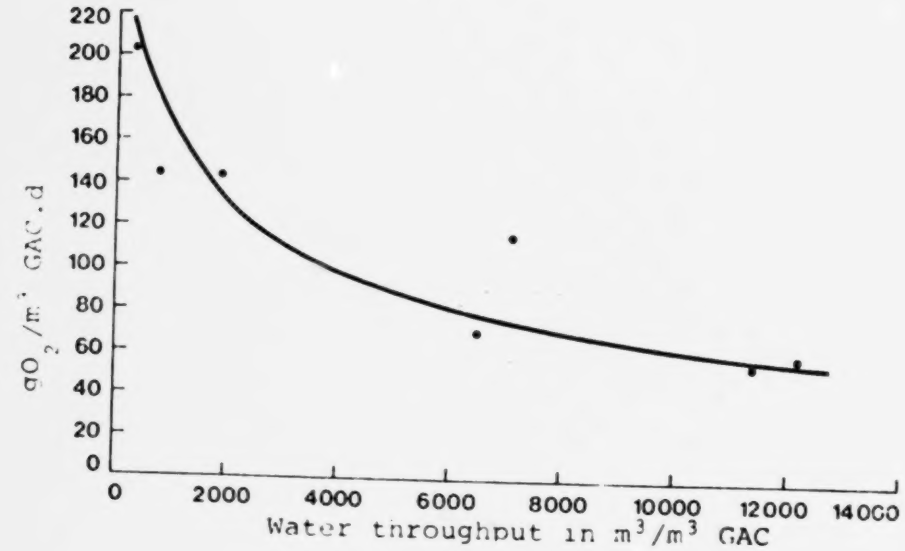


Fig. 5 Oxygen consumption in GAC filters as a function of the water throughput

This unfavourable effect of the proportion of difficultly degradable substances explains why much time and effort is spent on reducing this proportion by treatment with ozone. A preliminary oxidation of this kind is also carried out in Düsseldorf, but it is apparently insufficient to prevent the decreased oxygen consumption.

An example of the effects that can in principle be expected from a preliminary oxidation in the breakthrough curves is shown in Fig. 6.

According to this, when a small amount of ozone has been added a clearly more favourable breakthrough curve is obtained, since a part of the resistant organic material becomes biologically degradable as a result of ozonization, so that the previously mentioned enrichment of the difficultly degradable materials on carbon does not occur to the same extent as in the absence of such preliminary treatment.

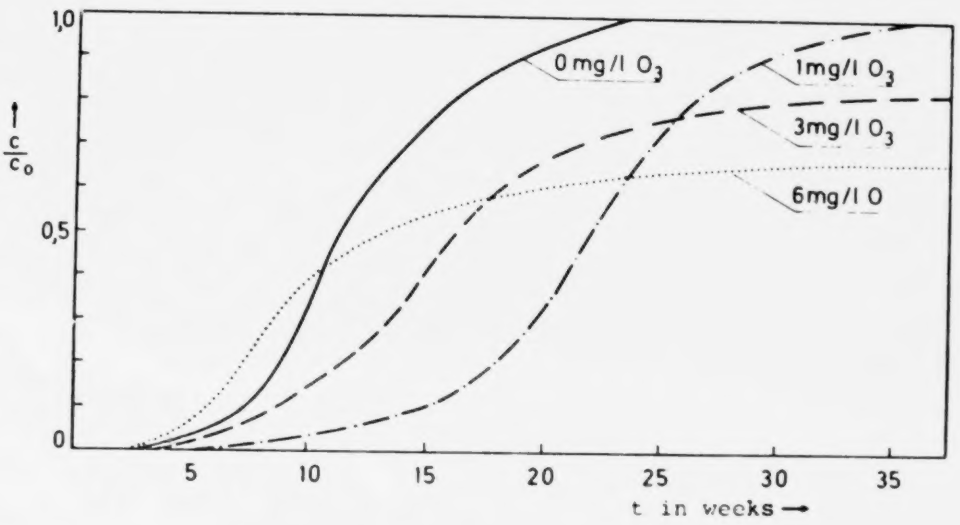


Fig. 6 Example of the changes in filter breakthrough curves with different ozone doses

Nevertheless, ozone oxidation, particularly when carried out with excessive ozone doses, can also modify the adsorbability of the organic substances. Thus, the more strongly polar substances produced by ozonization are often adsorbed less well. In extreme cases, as can be seen from the curve in Fig. 5 for an addition of 6 mg O_3/1, this effect can cause the initial breakthrough to occur at the same time,or under unfavourable conditions even earlier, than is the case when no ozone has been added at all. Only with very long running times and higher residual concentrations does this method become advantageous again with high ozone doses.

Readily degradable organic compounds are often produced, when high doses are used in this way, such as acetic and oxalic acid (7). These are immediately biologically oxidized on the outer surface of the activated carbon and are thereby rapidly and extensively removed. Under such conditions the breakthrough curves obtained basically follow the curve for

1 mg/l of ozone, and later pass into one of the curves for a higher ozone dose. Although the filter activity is enhanced under such conditions for all ozone doses, excessive doses of ozone are undesirable from the economic point of view.

This model explanation and clarification of the possible relationships shows why in practice very different effects are observed in dependence on the water quality, the filter dimensions, the properties of the carbon, and the amount of ozone used. For this reason the discussed combination of chemical and biological oxidation is not a treatment that can be performed universally and on all waters with equal effect and always following the same procedures. Moreover, since the possible dependences can seldom be obtained from simple laboratory tests, the performance of semi-technical trials is nearly always necessary.

If a summary of the essential criteria that can be deduced from the existing experience is nevertheless to be attempted, despite the above mentioned complexity of the situation in this oxidation process, the values given in the following table are obtained.

TABLE 1: Process parameters for biologically adsorptive treatment of drinking water

Ozone dose	0.5 - 1.0 g O_3/g DOC
Biological oxidation	100 g DOC/$m^3 \cdot d$
O_2 demand (for DOC oxidation)	200 g $O_2/m^3 \cdot d$
Residence time in filter presumed empty	15 - 30 min

Accordingly, 0.5 - 1 g of ozone is generally required per g DOC. Larger amounts are almost invariably disadvantageous if a different effect is to be avoided with the ozone. In nearly all of the filters studied so far an increase in the amount of CO_2 was found in the filter outflow under these conditions, corresponding to a DOC of 100 g per m^3 of filter volume and per day. As a rule, 200 g of oxygen per m^3 of the filter volume per day are necessary for this oxidation of organic substances. If NH_4 oxidation is taking place in the carbon filter at the same time the oxygen consumption becomes considerably higher, but the CO_2 production is thereby usually only slightly influenced.

The length of the residence time in the filter normally determines the time between two regenerations. If it is so long that, calculated on the carbon, the incoming organic substance corresponds in amount to the biologically oxidized substance, a biological filter can theoretically remain in use indefinitely, needing only a back-wash from time to time.

However, in practice the effectiveness of biological purification nearly always deteriorates as a result of the accumulation of resistant materials on the carbon surface. Toxic water constituents and their accumulation can also have an adverse effect. For this reason the running time of biological activated carbon filters is nearly always only some 5 - 10 times as long as that in the case of pure adsorption. The prolongation factor decreases with decreasing residence time.

Since the amount of CO_2 produced can be measured just as easily as the DOC decrease and the oxygen consumption, the most expedient operating parameters can be obtained for every individual case on the basis of the results with an experimental filter, the establishment of the optimal ozone dose being often the main difficulty. In an evaluation of the experimental results from biological activated carbon filters it is therefore advisable to observe and check the relationships mentioned above.

If, after an ozone oxidation, the measurements and operation of biologically adsorptive activated carbon filters are carried out in this manner, the combined process can prove to be a valuable aid in producing unimpeachable, naturally pure drinking water.

(1) MAIER, D.
Wirkung von Ozon auf die gelösten organischen Substanzen im Bodenseewasser
Vom Wasser 43 (1974), 127

(2) KURZ, R.
Untersuchungen zur Wirkung von Ozon auf Flockungsvorgänge
Dissertation, Universität Karlsruhe (1977)

(3) SONTHEIMER, H., WÖLFEL, P.
Amelioration de la degradation biologique des eaux residuaires par un traitement à l'ozone
Tagungsbericht Internat. Ozon-Kongress, Paris
4 - 6 Mai (1977)

(4) EBERHARD, M., MADSEN, S., SONTHEIMER, H.
Untersuchungen zur Verwendung biologisch arbeitender Aktivkohlefilter bei der Trinkwasseraufbereitung
Engler-Bunte-Institut der Universität Karlsruhe, Veröff. des Bereichs und des Lehrstuhls für Wasserchemie (1974), 7

(5) EBERHARD, M.
Erfahrungen bei der Anwendung biologisch wirksamer Aktivkohlefilter
Engler-Bunte-Institut der Universität Karlsruhe, Veröff. des Bereichs und des Lehrstuhls für Wasserchemie (1975), 9, 283; English translation: EPA 600/9-76-030 (1976)

(6) SONTHEIMER, H., HEILKER, E., JEKEL, M.R., NOLTE, H., VOLLMER, F.-H.
The Mülheim Process
J. AWWA (1978), 393

(7) GILBERT, E.
Reaction of ozone with substituted aromatics and with their oxidation products
Proc. of workshop on ozone and chlorine dioxide, Cincinnati, Ohio, Nov. (1976)

EXPERIENCE WITH BIOLOGICAL ACTIVATED CARBON FILTERS

M. Jekel

Introduction

The results presented here and the experience with the use of biological activated carbon filters originate from a common BMFT research project of the Rheinisch-Westfälische Wasserwerksgesellschaft (RWW) in Mülheim/Ruhr and of the Engler-Bunte-Institut in Karlsruhe. The object of the investigations was to replace the classical process used for the treatment of water of the river Ruhr - breakpoint chlorination, flocculation, and sedimentation, gravel and activated carbon filtration and sand bank filtration - by a direct process in technical plants, so that the high degree of chlorination with its disadvantageous effects on the water quality could be avoided. On the basis of the experience in waterworks at the lower Rhine (1,2) and of investigations at the municipal works in Bremen (3) the solution to the problem was seen in a combination of chemical oxidation with ozone and biological-adsorptive treatment in activated carbon filters (4).

Results from the pilot plants

Practical experience with this treatment was obtained both at an experimental plant at Dohne waterworks of the RWW, which had been running for two years, and at the main Dohne plant itself, which had been converted to the new process 15 months ago (5).

In the pilot plant Ruhr water was treated by flocculation, sedimentation, ozonization, and rapid filtration, and was passed through several activated carbon filters, various types of carbon being tested. In a smaller pilot plant, working in parallel, highly chlorinated flocculate discharge from the main plant was similarly treated with ozonization, rapid filtration, and activated carbon filtration. The results of this parallel trial are shown in Fig. 1.

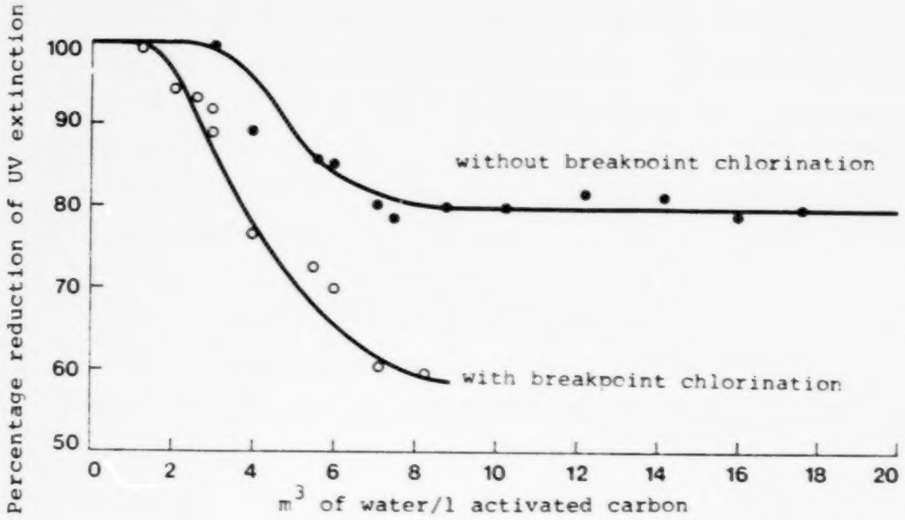


Fig. 1 Influence of breakpoint chlorination on the effectiveness of water treatment with flocculation and sedimentation, ozonization, filtration and activated carbon treatment (2.5 m at 10 m/h)

This figure gives the percentage reduction of the UV extinction at 254 nm, as a measure of the removal of organic substances in the whole treatment process, against the throughput in m^3 per litre of activated carbon. The early breakthrough of the GAC filter with preceding breakpoint chlorination is a consequence of the high loading of the activated carbon with organic chlorine compounds, which hinders the development of an effective biological activity in the filter. Without breakpoint chlorination, however, an essentially better water quality was obtained, caused by the effective microbial processes in the activated carbon filter. These processes also ensured that, over a period of about 14 months, the effectiveness of the treatment remained essentially constant at 75 %, i.e. the upper curve in the illustration can be extended to 40 m^3/l activated carbon (5).

The biological oxidations in the GAC filter can be balanced over the chemical parameters DOC, inorganic carbon, ammonia, and dissolved oxygen. The following table shows as an example the variation of these four parameters in the GAC filters of the pilot plant for the winter months January to March 1977 with low water temperatures and a relatively high ammonia loading.

TABLE 1 Biological activity in activated carbon filters at low temperatures

Activated carbon	$-\Delta$DOC ppm	$+\Delta$anC ppm	$-\Delta NH_4$ ppm	$-\Delta O_2$ ppm
LSS 2,5 m	1,1	1,0	1,43	7,2
ROW 2,5 m	1,2	1,1	1,41	7,2
NK 12 2,5 m	1,0	1,2	1,45	7,1
F 400 2,5 m	1,3	1,2	1,43	7,1
BKA 2,5 m	1,2	0,9	1,44	7,1
LSS 5,0 m	1,6	1,2	1,46	7,7
ROW 5,0 m	1,7	1,3	1,47	7,7
Mean values:	Jan.-Marz 1977			
Mean water temp.:	6,8 °C			
Inflow (gravel filtrate):	2,6 mg/l DOC 1,53 mg/l NH_4			

In the first 2.5 m of the filters, which operate at 10 m/h, the amount of DOC removed is in general only a little greater than the production of inorganic C, i.e. during this period most of the organic substances removed were biologically mineralized. At the same time an almost complete nitrification of the ammonia took place, which was also responsible for the high oxygen demand. In the second half of the 5 m filters, however, the organic material was still predominantly removed by adsorption, as was detected by the differences in Δ DOC and Δ inorg. C.

It is worth noting the really small differences in the biological activity of the activated carbons tested, which, however, showed considerable differences in their adsorption capacity. Moreover, further observation of the activated carbon filters at the pilot plant showed that the nitrification had virtually no effect on the biological oxidation of the organic compounds. Furthermore, no significant influence of temperature on the biological activity could be observed in the pilot plant.

The breakthrough behaviour of biological activated carbon filters is influenced, among other things, by the adsorbed biologically resistant substances. Both the removal performances of the pilot plant filters in g DOC/m^3 activated carbon per day and the total loadings of the activated carbons for the first 18 months of operation are given in the following figure.

In addition, the removal performance was divided into a biological oxidation component and an adsorption component, calculated from the carbon loading. As shown in Fig. 3, an average of about 75 % of the organic substances removed is biologically oxidized, while the remainder, predominantly resistant compounds, is adsorbed. Owing to the enrichment

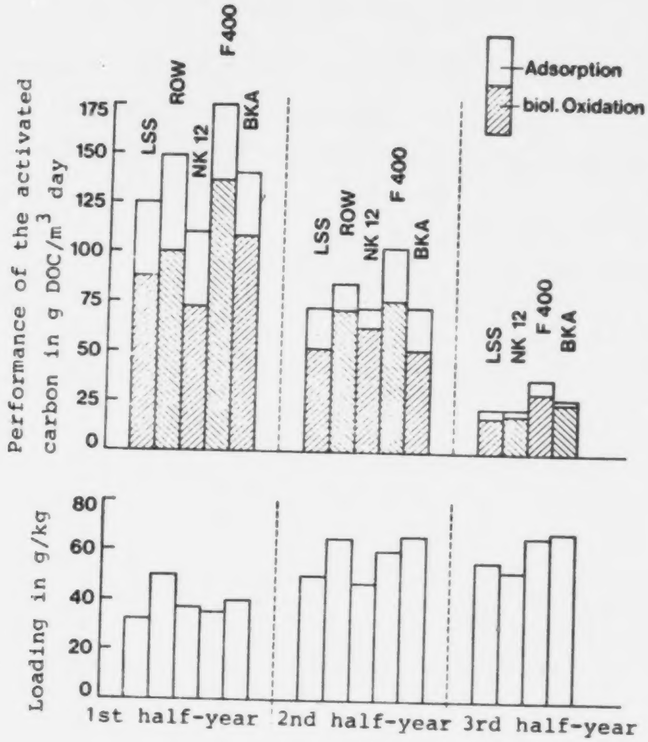


Fig. 2 Performance and loading of biological activated carbon filters

of these compounds, recognizable by the increasing loading of the activated carbon, the performance of the filters clearly falls off, particularly in the third half-year period. Simultaneously, a clear improvement in the quality of the raw water occurred, so that the DOC in the influx was decreased from about 2.5 to 1.8 ppm. This certainly also intensifies the decrease in performance. The measurement results indicate that the degradable substances are at first adsorbed and only then biologically mineralized. The relatively high proportion of about 75 % of biologically oxidized substances furthermore permits the conclusion that the operating time of biological activated carbon filters in the treatment of Ruhr water is prolonged by a factor of approximately 4 in comparison with pure adsorption.

Experience with the treatment at the Dohne waterworks

On the basis of the results with the pilot plant, the Dohne waterworks were converted to the new treatment process in the spring of 1977, as shown in the following flow diagram (4):

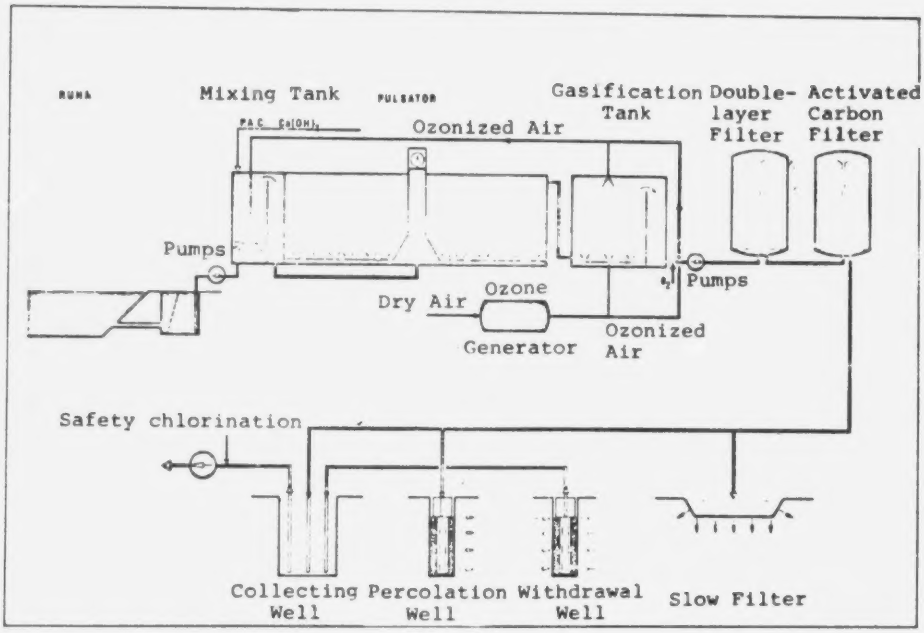


Fig. 3 Flow diagram of the Dohne works

The Ruhr water is directed into a small mixing chamber for preliminary oxidation with about 1 ppm of ozone. Polyaluminium chloride is added at the same time for flocculation. The preliminary ozonization with an immersion gas tube results in clear water after the solids have been removed in a pulsator. On average about 2 ppm of ozone are introduced into the gasification chamber. If necessary, additional pure oxygen can be mixed in before the filters to cover the consumption in the subsequent rapid and activated carbon filters. The bed length of the activated carbon filters was increased from 2 to 4 m to maintain a sufficient residence time at a velocity of 22 m/h. These were set into operation in November of last year with virgin activated carbon.

The following table shows how the conversion to the new treatment affected the quality of the drinking water.

TABLE 2 Effectiveness of classical and new treatment at Dohne waterworks, RWW, Mülheim/Ruhr

New treatment, without activated carbon filter (July-Oct.1977)	UV Ext. m^{-1}	DOC mg/l	NH_4^+ mg/l	Colony count/ml	E.coli/ 100 ml
Ruhr	8.6	4.0	0.79	9630	1550
after flocculation	4.9	3.3	0.43	3510	16
after ozonization	3.2	3.1	0.43	-	-
after filtration	3.1	2.7	0.03	1440	1
after soil passage	2.3	1.2	0.01	19	<1
Classical treatment (1975)					
Ruhr	6.8	4.0			
after flocculation	4.5	3.2			
after ozonization	4.4	3.2			
after activ.carbon	4.0	3.0			
after soil passage	3.1	1.8			

The mean values of some parameters in the new treatment without activated carbon filters are compared here with the values of the earlier classical process in 1975, when the quality of the untreated water was similar. The oxidation effect of the ozone is noticeable, by means of which resistant material is converted to biologically degradable substances. The improved purification effect of the soil passage is also due to this factor. The fact that the rapid gravel filters are also biologically active is obvious from the extensive reduction of ammonia and the re-population of the filtrate with bacteria. The numbers of colonies decrease in the soil passage to two-digit numbers, since the degradable substances have been practically completely removed.

With the inclusion of the enlarged activated carbon filters a large proportion of the purification effect of the soil passage was shifted to the plant. The behaviour of the newly installed large filters is shown in the following figure, in which the mean values of the removed DOC and the inorganic carbon formed in the whole activated carbon filtrate are plotted against the time of operation.

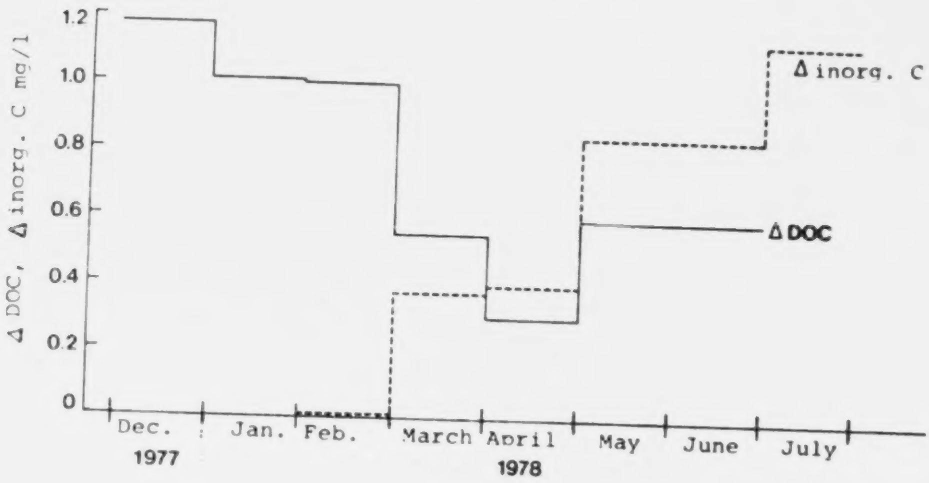


Fig. 4 Behaviour of the newly installed biological activated carbon filter at Dohne waterworks

In the first three months with the water temperature below 8 °C the activated carbon filters showed practically no biological activity. The Δ DOC values indicated a really early breakthrough of the organic substances, since the carbon was already becoming increasingly loaded. With the higher concentrations of adsorbed degradable substances and with rapidly rising temperatures in the spring the biological oxidation set in, which from May clearly covered the substance already adsorbed. The activated carbon was regenerated biologically and from this month on displayed an improved purification effect.

Exhaustive investigations on the bacteriological nature of the activated carbon filtrate were carried out in the large plant, because this aspect plays an important role in a direct input into the distribution network. Since four types of activated carbons with different adsorption capacities were used in the large plant, the filtrates showed sometimes considerable differences in the DOC values. The effect of this on the colony counts determined in parallel (incubated for 48 h at 22 °C on nutrient gelatine) is shown in the following figure.

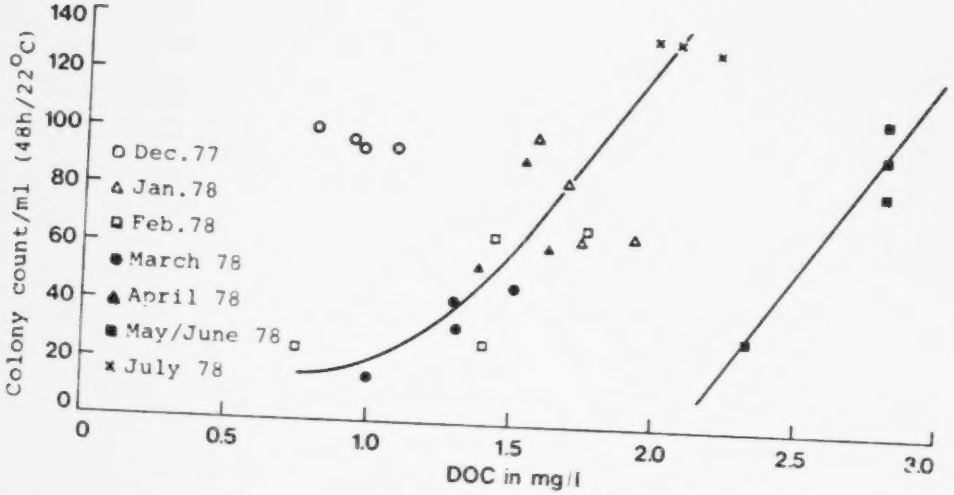


Fig. 5 Influence of the DOC in the filtrate of biological activated carbon filters on their bacterial population

The geometric mean monthly colony counts are here correlated with the corresponding mean DOC values of the individual carbon filtrates. While in the first month of operation, December 1977, with still scarcely any developed biological activity, no relation between bacterial population and the DOC can yet be distinguished, in the following months with increasing biological activity of the active carbon filters a dependence of the bacterial population on the organic loading of the filtrate is established. Remarkably, greater deviations appear in May and June, when a different composition of the organic substance during the growth of algae was clearly present. From these results it may be concluded that a larger proportion of biologically resistant compounds occurred at this time.

From these results it follows that a good adsorbing activated carbon, which also removes degradable substances more efficiently, produces lower colony counts in the filtrate. The mean values themselves show predominantly two-digit and three-digit colony counts. However, if the ozone dosage is increased, the experience with the Dohne waterworks indicates that the bacterial counts become considerably higher.

A natural far-reaching elimination of bacteria from the activated carbon filtrate can still be achieved, according to trials with a rapidly operating slow sand filter, at a velocity of 2 m/h, the colony counts being then reduced on average to single-digit values (6).

With the development of an effective microbiological activity in the spring and summer of this year, a mass development of nematodes was observed in the rapid and active carbon filters. The reasons for this are to be found mainly in the long running times of the gravel filters, which, because of the very good quality of the clear water after flocculation, were one week. On the other hand, for technical reasons the gravel filter in the Dohne plant could be backwashed only with the relatively low speed of 20 m/h.

According to running experience, this problem can be solved by frequent washing of the filter, so that the running time should not be more than four days, the reproduction cycle of nematodes. This applies above all to the time of increased water temperatures in the summer, when a continuous observation of the backwash water is recommended to prevent a mass development by frequent and vigorous backwashes. However, the back-flushing speed should not be so high that the microbiological activity of the filters is impaired.

Summary

The experience with biologically working activated carbon filters in the treatment of Ruhr water can be essentially summarized in the following points:

1) The high biological activity of the activated carbon filters prolongs the running time about fourfold in comparison with pure adsorption.

2) The bacteriological nature of the activated carbon filtrate will be satisfactory when a far-reaching removal of biologically degradable substances is achieved.

3) Reliable operation of biological filters can be achieved by means of a suitable backwashing technique.

(1) HOPF, W.
Versuche mit Aktivkohlen zur Aufbereitung des Düsseldorfer Trinkwassers
gwf-Wasser/Abwasser 101 (1960), 14, 330-336

(2) HOPF, W.
Zur Aufbereitung mit Ozon und Aktivkohle
gwf-Wasser/Abwasser 111 (1970), 13, 156-164

(3) EBERHARDT, M., MADSEN, S., SONTHEIMER, H.
Untersuchungen zur Verwendung biologisch arbeitender Aktivkohlefilter bei der Trinkwasseraufbereitung
Publication Wasserchemie, Engler-Bunte-Institut, Univ. Karlsruhe 7 (1976); gwf-Wasser/Abwasser 116 (1975), 6, 245-247

(4) SONTHEIMER, H., HEILKER, E., JEKEL, M.R., NOLTE, H., VOLLMER, F.H.
The Mülheim Process
J. AWWA 70 (1978), 393-396

(5) HEILKER, E., JEKEL, M., SONTHEIMER, H.
Biologisch-adsorptive Trinkwasseraufbereitung in Aktivkohlefiltern
DVGW-Schriftenreihe Wasser, Nr. 101, zum BMFT-DVGW-Statusseminar "Neue Technologien, Hannover, Jan. 1978
To be published

(6) SCHALEKAMP, M.
Die Wirksamkeit von schnell betriebenen Landsamsandfiltern
Publ. Wasserchemie, Engler-Bunte-Institut, Univ. Karlsruhe, 5 (1971), 3, 49-66

THE USE OF COMBINED CHEMICAL AND BIOLOGICAL OXIDATION PROCESSES

P. Schulhof

Before I talk about the processes combining chemical and biological oxidation I should like to dwell briefly on what I would say about the papers given in the course of this symposium if I were one of the men responsible for the construction or modernization of the drinking-water-treatment plants in France.

I would first have remarked on the incredible advances in analytical methods in recent years. I would have been particularly surprised by the absolutely thorough knowledge attained within a very short time with the aid of these methods on the subject of the oxidation of polluted water.

However, my enthusiasm would have been somewhat dampened by the fact that the majority of cases dealt with studies on isolated products or substances, while many of the speakers have made reference to the competition situations that can arise in the course of oxidation reactions in mixtures. Let us not forget that raw river water is a particularly complex mixture!

However, the agreement of the presented results and in particular of the questions that have been put would have disturbed me too. My concern would have been intensified by the fact that the sanitary and hygienic significance of all the by-products mentioned is still far from known. After several years we are still debating about the simplest of them, chloroform and, according to your remarks this represents only the tip of the iceberg.

It must be added that the industry evolves new compounds from year to year, indeed at least as many as those that have been mentioned during the last three days.

On the other hand, my concern would have been somewhat abated by the consideration that the studies are often performed under extreme conditions: very severely polluted water such as Rhine water or oxidation with very massive doses as in the United States. The average reality in moderate France is perhaps less gloomy.

Finally, I would now perhaps understand better the wisdom of the German standards cited by you, recommending the use of waters low in man-made substances. Within the wider framework of the EEC I would also understand the reasons for the caution of the guidelines established in Brussels for the quality of the raw water about to undergo treatment.

To return to everyday matters in France, however, the construction of treatment plants must be developed further and the plants must be run with the water available. The plants for treating the severely polluted waters in the Paris area must be modernized. What must be done here?

From these days of study some rules have emerged clearly that normally should be a matter of plain common sense.

For example, the fact that in the case of a polluted water the first treatment process to be put into action should not be an aggressive oxidation. Therefore I would strive towards a gentler oxidation, i.e. biological, and one that is as natural as possible.

I concede that I do not have available a site suitable for a soil passage. These do exist in France, but by no means everywhere.

First of all I would investigate whether a storage reservoir can be installed for the raw water. This biological reactor - hardly mentioned this morning - is at once a clarifying tank and a safety stage, thus offering a whole series of simultaneous advantages.
If I had no room for a reservoir of this kind I would look for a different biological reactor, but which one? This would pose considerable problems.

Let us continue. A physical and chemical clarification line is put in. For the pre-oxidation I would use ozone in a moderate dose. After all, we have seen that preliminary ozonization is a logical supplement to flocculation.

Then there is the viricidal ozonization, still indispensable for the treatment of polluted water. Its logical supplementation was described this morning. This involves a second biological reactor that, followed by a weak final chlorination, should protect the network.

Perhaps I would have had certain difficulties in designing the ozonization with a minimal viricidal dose. I have maintained that the addition should be continuous, neither too strong nor too weak and extended over a really long period.

All this is very rough, and in my special case I would definitely construct a pilot plant, which would present no undue difficulties.

On the other hand, I would find it much more difficult to determine the biological reactor to be installed. For what is to be done when the problem is not one of modernizing an old plant that already makes use of slow sand filters or activated carbon filters?

It seems highly unlikely that when a new plant is to be built the slow sand filter technology designed almost a century ago in a completely different context or the activated carbon filter technology developed 30 years ago for the purposes of dechlorination and the prevention of undesirable taste are ideal for a biological reactor.

This is the real problem that I wished to come to with these lengthy preliminary remarks. The technology of chemical oxidation has apparently reached the age of maturity. The most recent of these techniques, ozonization, has grown up in France over the last 15 years. In my view the same cannot be said of the technology of the biological reactors, which is still in its infancy.

In the years to come we shall need at least two different types of such biological reactors, one for raw water and one for clarified water.

I believe this is the challenge that progress in analysis places before the technologists. Only when these developments succeed will the studies presented here make possible spectacular advances in the treatment of water.

The technology of the biological reactors could, and this is a thoroughly classical conclusion towards the end of a symposium,become the very likely and universally useful theme of another symposium.

A. Bousoulengas (Greece)

1. Most of Greece's small cities and villages use ground water for drinking purposes. In bigger cities surface water, or both ground and surface water is used.

2. Since 1958 chlorination has been established by Sanitary Regulation as the disinfection means for drinking water supplies. There should always be 0.2 mg/l free Cl_2 present at any point in the distribution network. This is checked regularly by taking samples from a number of points, depending on the size of the network in question.

3. Sanitary Regulation of 1968 "On the Quality of Drinking Water" determines the physical, chemical and microbiological characteristics that drinking water should have. It determines maximum allowable concentrations for various inorganic substances (Ag, As, Cd, Pb, F^- etc.) and organic substances as well.
Regarding organic substances and their products (NH_3, NO_3^-, NO_2^- etc.) there is a recommendation for their quantitative determination.

4. There are no regulations determining the treatment process. However, the above-mentioned sanitary regulation prohibits the use of a water source if it is found to contain a series of substances in concentrations higher than those determined by the regulation. These substances include sulphates, carbonates and other inorganic substances and organic ones such as detergents and phenolic compounds.

5. Research is carried out by various state institutes and university laboratories on mainly applied problems concerning drinking water.

6. If a water source is found suitable for drinking use, restrictions are applied by regulation or decree prohibiting the discharge of any effluents or the disposal of any materials into the source or into the waterways feeding this source - lake etc.

L. Coin (France)

QUALITY OF RAW WATER:

France is trying to use raw water of adequate quality. However, as a result of modern developments and changes in the habits of the consumer in our industrial society - despite the fierce battle being fought against environmental pollution - certain correcting measures seem inevitable. They would be:

- either on a quality level, generally by choosing different locations as raw water sources, or by making new water reserves accessible;
- or on a treatment level, by reconstructing existing plants and by introducing the most recent adsorption agents, or by modified oxidation processes.

We are therefore awaiting with interest the realization of joint regulations on the quality grade of raw water permitted to be used for drinking-water treatment.

REGULATIONS ON THE CONTROL OF DISINFECTION

There are two forms of control:

1. performed on-site by the waterworks;
2. spot-checks carried out by the Department of Public Health. Dates and guidelines are laid down by the C.S.H.P.F. (Conseil Supérieur d'Hygiène Publique de France).

On account of the special guidelines on maximum concentrations of micro-pollutants and similar substances, drawn up in Brussels but not in force yet, France has modified the regulations. These modifications have partly been legalized already, for instance concerning those regulations which were only slightly changed, e.g. for heavy metals. Organic micro-pollutants, not mentioned previously, are now included in the programme of treatment plants in densely populated towns.

NECESSITY AND VALUE OF SAFETY CHLORINATION:

This is a controversial question. In smaller residential areas drinking water is supplied to the consumer without previous treatment, taking into account water protection areas and issueing certain restrictions. In densely populated areas chlorine is added to the water. The real problem is subsequent chlorination after ozonization. In Paris, for instance, the excessive chlorine is neutralized again before distribution. Our ideas on microbial control will certainly have to be revised: Concerning fecal germs, the present strict control measures should be retained. Improvements seem necessary, however, in connection with the significance of the fluctuation of the saprophyt numbers. A chlorine content of 0.05 ppm to 0.1 ppm at the most, as it is laid down in France, covers short-period risks; it should, however, be increased in times of epidemics.

BREAKPOINT CHLORINATION - yes or no?

After having been in use for many years, breakpoint chlorination is about to be abolished in France - and with good reason.

REGULATIONS ON METHODS OF TREATMENT:

This is a complicated question. The Offices of Public Health decide on the type of treatment used for producing drinking water from raw water. However, this decree does not come into effect in those cases where the size of the project requires the decision of the C.S.H.P.F. This point in particular will be treated in the ruling still under consideration, in complete agreement with all parties concerned.

RULES FOR APPLICATION AND FUTURE RESEARCH:

All the various regulations have been taken very seriously in France, especially as concerns the treatment of raw water. Questions concerning the distribution network are governed at present by hygiene regulations of the Departements. This presents a serious shortcoming, which will surely be overcome in the future.

As far as research is concerned, the various methods of treatment, their development and improvement remain very important. Epidemology will forcibly include the effects of the distribution system on the water quality at the consumer's tap, and here the responsibility also lies with the consumer himself, because he uses the water supplied to him and thereby changes the quality himself. This is a decisive point, and the quality of the material used for domestic plumbing is also gaining importance in this connection.

T.A. Dick (United Kingdom)

1. Sources and Treatment of Water

In the United Kingdom, one third of the potable water is derived from underground supplies, one third from upland surface supplies (lakes, reservoirs and streams) and one third from lowland rivers. The proportions vary considerably in different parts of the country and in the drier eastern areas there is little choice but to draw water from rivers which may contain a substantial proportion of waste water, that is, water which has passed through a sewage treatment plant. Sewage treatment plant effluents are not chlorinated before being discharged to UK rivers.

Underground water supplies and upland surface water supplies are generally of high quality and require only the conventional treatments. For surface waters from lowland rivers it is recommended practice in the UK to store the water in reservoirs, as a safeguard against fluctuating river flows, possible accidental contamination and to obtain self-purification benefit. The water then receives treatment by slow sand filtration, or coagulation and rapid gravity filtration or both. The water then passes to a closed service reservoir before distribution or may go directly into supply. Pre-chlorination treatment of the raw water before or during treatment is fairly common.

With few exceptions, all public water supplies in the United Kingdom are chlorinated after treatment by conventional methods. As a general policy, the degree of final chlorination is such that 0.1 to 0.2 mg/l of free chlorine remains at the end of 30 minutes contact.

2. Quality of Water

There are, at present, no mandatory standards in the UK for the quality of water put into supply other than that the water shall be 'wholesome', which is generally accepted as meaning "clear, palatable and safe". In practice, the quality of water put into supply follows the recommendations of the 1970 World Health Organisation European Standards, and for bacteriological quality, the recommendations given in a UK Government document Report 71, "The Bacteriological Examination of Water Supplies". There are no mandatory regulations for plate counts for drinking waters in the UK. However, plate counts are carried out by many of the water suppliers to assess changes in the general quality of water in the treatment plant and supply system, particularly when the raw water has been derived from surface sources. The 37^{o} plate count is generally used as pollution indicator but the total plate counts at 22^{o} were of particular value during the 1976 drought year to ensure that there was no in-leakage of contaminated water into distribution mains.

3. Present UK Policy

The United Kingdom is well aware of the work discussed at the present Conference but its approach to the establishment of water regulations and policy is at present directed more to establish whether a health risk exists, rather than making any fundamental change in treatment policy into unknown areas of risk. The UK is well situated for such research. It has a wide variety of situations where there is reuse of water and where the Water Research Centre and the 10 Regional Water Authorities have accumulated extensive data on water quality. We have excellent health data accumulated over many years and we have an intensive programme on micropollutant identification and mutagenic screening of waters and concentrated water samples. Detailed statistical examination of the data is actively in progress. There is also a national programme for the determination of trihalomethanes in drinking water.

We believe this type of work is of fundamental importance in establishing whether our policy on reuse of water and on chlorination is sound. It is encouraging to note, for example, that the national data for the incidence of death from cancer of the stomach and the bladder have fallen significantly between 1970 and 1975 for adults between 45 and 64 years. I should also add that the UK has another drinking water problem concerning reduction of lead, primarily in the older houses with lead pipes in soft water areas, and at present, we regard this as our number one priority for action.

4. Catchment Control

As a final point, the UK believes that there is considerable advantage in reducing the input to raw water sources of organic materials rather than trying to remove them from the water during the treatment process. Some of the UK Water Authorities are now intensively monitoring the use of organic materials in factories, to see what is used in the process and what can be lost from the process during manufacture. At the same time, the effluents leaving the plant and the sewage works are analysed and also the river itself to establish a 'balance' on the 'missing' organic material. The amounts can be small but very significant. Each type of industry is being examined, and attention will also be given to commercial bodies (e.g. laundries, dry-cleaners etc) and to the domestic use of chemicals. The system, known as catchment control, requires a great deal of patient work but can be very successful in reducing undesirable micropollutants from factory processes, particularly where less harmful materials can be used in the process.

E. Heinonen (Finland)

The water supply of the largest towns in Finland is dependent on surface water sources. In treatment the water passes through coagulation with aluminium sulphate at a suitable pH (≈ 6), clarification and rapid sand filtration. Chlorine is the chemical used for disinfection and generally also for the oxidation of substances affecting taste and odor.

The ammonia content in river waters, used as raw water supplies and carrying a pollution load of domestic wastewaters, rises in the winter to such values that breakpoint chlorination of NH_4 is necessary. Also spring runoff from fields during the flood period causes taste and odor disturbances that are not removed by treatment process. They are reduced by superchlorination and the use of powdered activated carbon. Blooms of algae and microorganisms in lake basins especially in the summer often cause taste and odor disturbances in normally treated drinking water. Chlorine dioxide has been used to eliminate these and experiments have even been made with $KMnO_4$ instead of, or in addition to chlorine oxidation. The most effective way of combating algae in watercourses and at water intakes has proved to be treatment with copper sulphate.

The Finnish National Medical Board has given standards for drinking water; these were last revised in 1971. They are principally based on the international drinking water standards of WHO dating from 1963 with a few points taken from the WHO European area standard of 1970. Of special interest with regard to the conditions prevalent in Finland are the norms for $KMnO_4$-consumption in order to limit organic matter in the water (lower limit 20 mg/l and upper limit 40 mg/l), for NH_4 as an indicator of pollution (0.2 and 0.5 mg/l), as well as for Al-residue, characterizing the treatment process (0.5 - 1.0 mg/l). Of organic compounds limits have only been set for phenols and anionactive detergents, but not for example for biocides or any of the general parameters (e.g. CCE, TOC).

The bacteriological standards give limit values to fecal streptococci in addition to coliforms and thermotolerant coli bacteria.

The most common difficulties in surface water treatment are due to the water's fairly high humus content, sometimes also to similar effects caused by wastewaters from pulp production in the wood-processing industry. The removal of organic matter is incomplete in Al-coagulation (TOC residue >4 mg/l) and a fair amount of aluminium remains in the water (>0.3 mg/l); the high chlorine demand and its corresponding use result in the formation of considerable amounts of organic chlorine compounds observable both as taste and odor disturbances as well as the incidence of $CHCl_3$ (>50 μg/l), observed in analyses. Taste and odor problems are intensified during the winter time with break-point chlorination to destroy the ammonia. Similar problems are experienced sporadically also during periods of spring flood and warm summers.

The measures used at the major waterworks in Finland to solve problems arising in water treatment are principally the following:

1. Improving the quality of the raw water sources in use

Water conservation, dilution with water transferred from neighboring watercourses, and impoundment before taking the water into treatment plants have been the methods most commonly used. All of the above-mentioned have been used especially by Helsinki City Waterworks.

2. Transferring water intake to sources of a better quality

The numerous lakes in Finland form alternative water supplies of good quality and abundant quantity to the polluted river or lake waters presently in use. The Helsinki metropolitan area on the southern coast as well as several communities north of it are presently engaged in a project of constructing a rock tunnel 120 km long from the southern end of Lake Päijänne, a large lake basin in Central Finland. The tunnel will be completed in 1982. Several other smaller water transfer projects have been completed or are in the planning stage for the water supply of other major Finnish cities.

3. Improving present treatment methods

The methods mentioned above for the improvement of raw water quality already aim at diminishing the substances causing taste and odor as well as other disturbances in drinking water. The treatment process proper has been improved both by increasing the effectiveness of chemical treatment (increased use of activated carbon and chlorine dioxide) and by making changes in the order of the various phases of the process so that the formation of disturbing substances has been diminished (e.g. decrease in the formation of chlorinated hydrocarbons by transferring the main chlorination point to after coagulation and filtration).

4. Developing new treatment methods

The trend is to substitute chlorine oxidation with ozonization. Helsinki and its neighboring municipalities will begin ozone treatment already in 1979. Several other towns are at present carrying out study programs on its use or are contemplating the starting of such programs in the near future.

Activated carbon filtration after chlorine oxidation has been studied with large-scale pilot plant test runs in Helsinki and its introduction is at the moment studied at Turku, one of the largest cities next to Helsinki, to relieve local water treatment problems.

The test runs in Helsinki showed as drawbacks for the method the rapid decrease in adsorption capacity (during a run of 3-5 months) showed by measurements, and a corresponding rapid deterioration as well as large fluctuations in taste and odor characteristics. This led to the decision to abandon this method of quality improvement and to adopt ozonization, which had consistently given good results in the test runs, as an additional method to make the treatment process more effective.

Victor J. Kimm (U.S.A.)

Legislative control of contagious or infectious disease first began in the United States with the National Quarantine Act of 1878. Regulations developed under this Act were intended primarily to maintain sanitary drinking water aboard vessels. However, in 1912, due to severe outbreaks of intestional disease among passengers aboard steamships on the Great Lakes, the Treasury Department issued rules which required State certification that drinking water aboard interstate vehicles would not cause disease. This concept became the basis for the 1914 Treasury Standards and the subsequent modifications knows as the U.S. Public Health Service Drinking Water Standards.

Early in 1968, a series of bills were introduced in Congress for the general protection of drinking water. Eventually the Safe Drinking Water Act of 1974 was passed, and it applies to all public water systems serving 25 persons or more on a regular basis, for a total of about 200,000,000 Americans. This Act mandates the U.S. Environmental Protection Agency to develop primary drinking water regulations containing maximum contaminant levels for microbiological, chemical and radiological constituents that affect the public health.

NATIONAL INTERIM PRIMARY DRINKING WATER REGULATIONS

The Interim Regulations establish Maximum Contaminant Levels (MCL) for coliform bacteria, turbidity, ten inorganic chemicals, six pesticides and radiological contaminants (Table 1). As of June 24, 1977, water utilities are required to conduct periodic monitoring at a prescribed frequency to ensure compliance with

TABLE 1 The maximum contaminant levels for constituents in the National Interim Primary Regulations

Constituent	Level mg/l unless specified
Biological Parameters	
Coliform bacteria	1 per 100 ml (mean)
Turbidity	1 NTU (Waiver to 5 NTU possible)
Inorganic Chemicals	
Arsenic	0.05
Barium	1
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10
Selenium	0.01
Silver	0.05
Fluoride	1.4-2.4[x]
Organic Chemicals	
Endrin	0.0002
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
2,4D	0.1
2,4,5TP Silvex	0.01
Radionuclides	
Radium 226 and 228 (combined)	5 pCi/l
Gross alpha particle activity	15 pCi/l
Gross beta particle activity	4 millirem/year

[x] Based on annual average air temperature

the regulations and to notify the public if the standards are exceeded. The Safe Drinking Water Act also provides that States will develop their own regulations and some States have more stringent requirements than those in the Interim Primary Regulations.

The Maximum Contaminant Levels for coliform bacteria and turbidity are essentially those contained in the 1962 Public Health Service Standards (Table 2). It is generally agreed that these MCLs are adequate to protect the public from infectious disease transmitted by recent fecal contamination; however, there is data to suggest that the coliform testing procedures may not be entirely effective as an indicator of certain diseases of viral and protozoan etiologies. The apparent problem with the indicator procedures is not whether those particular disease-producing organisms are found in water contaminated with fecal material, but rather that a number of viruses and protozoans can survive in water for longer periods than the coliform indicators. Some viruses and protozoans also seem more resistant to disinfection than coliforms.

At the present time there are no national disinfection standards in the United States. Drinking water disinfection is not mandatory nor are there restrictions on the quantity and type of disinfectant that can be used. The MCL of a monthly mean of 1 coliform/100 ml is the sole measure of microbiological quality, but the means of achieving acceptable coliform levels are not prescribed. Monitoring frequencies based upon the size of the population served range from a minimum of 1/month for populations of less than 1000 to 500/month for populations larger than 4,690,000. There is, however, a provision in the Interim Primary regulations that allows

TABLE 2 Provisions in the National Interim Primary Drinking Water Regulations affecting the presence of microorganisms

1. Coliform bacteria - 1 coliform/100 ml of water
    a) A supply may substitute chlorine residual determinations for not more than 75 % of the required number of coliform analyses if 0.2 mg/l free chlorine is maintained.

2. Turbidity - 1 nephelometric turbidity unit (NTU). The State may allow up to 5 NTU if water does not cause a risk to health and the increased turbidity does not:
    a) interfere with disinfection;
    b) prevent maintenance of an effective disinfectant agent throughout the distribution system;
    c) interfere with microbiological determinations.

States to permit the substitution of chlorine residual analyses for up to 75 % of the monthly coliform sampling requirements. If that option is selected, a free chlorine residual of at least 0.2 mg/l must be maintained. Should the chlorine residual fall below 0.2 mg/l, immediate sampling for coliform bacteria is required.

The value of disinfectants in controlling pathogens in water is unassailable, but, in one sense, disinfectants and their by-products, and particularly chlorine and chloramines, are contaminants of increasing public health concern. They are the most widely used synthetic chemicals in water treatment in the US and they are used at relatively high concentrations. EPA finds itself in a difficult position in prescribing controls because there is very little information currently available on the human toxicology of chronic exposure to disinfectant chemicals, their degradation products, or their reaction by-products with other contaminant chemicals in water. That is an appalling fact considering some of these disinfectants have been in use for over 60 years.

The issue concerning the misuse of disinfectants has become particularly acute in the past three years with the identification of chloroform and other trihalomethanes in chlorinated drinking water. But trihalomethanes are not the entire problem by far; it is only the relative ease of identification and quantification that has caused interest to concentrate on them. The trihalomethanes should be considered indicators of the existence of a host of undefined and perhaps undefinable oxidized and halogenated chemicals that are introduced as a result of chlorination. The same questions can be raised about any disinfectant under consideration, be it chlorine, chloramine, ozone, chlorine dioxide, or iodine.

The Environmental Protection Agency has recently proposed regulations to limit trihalomethane concentration aimed at minimizing risks from unnecessary exposure to the by-products of the disinfection process. High doses of disinfectants should not be used to provide chemical oxidation treatment unless it is part of another process which would control the chemical by-products produced. In high organic water, water treatment processes should be applied that involve purification to reduce precursor levels before application of a disinfectant.

These proposed regulations further conclude that it is necessary to take steps to limit and minimize trihalomethanes in drinking water by means that would not interfere with the maintenance of pathogen control. The current proposed regulations include an initial limit on total trihalomethanes (the sum of chloroform, bromodichloromethane, chlorodibromomethane and bromoform) of 0.10 mg/l for approximately 400 public water systems serving populations greater than 75,000 persons. Only monitoring is required in smaller systems (10,000 to 75,000), and systems with less than 10,000 are not covered. The initial standard was selected based on current feasibility and is not to be construed as a "safe" level. This standard will be reduced and population coverage increased as experience is gained.

To assure that any steps taken to reduce THM concentrations in drinking water will not increase the possibility of microbial contamination, additional microbiological monitoring is proposed for a water system that is modifiying existing treatment practice. Standard Plate Count (SPC) determinations must be made at least daily both at the treatment plant and in the distribution system, for one month before and six months subsequent to the treatment change to assure that no degradation of water quality occurs. Analyses prior to any treatment change are intended to provide a baseline to which subsequent effects can be compared. The appropriate number and sampling locations of SPC analysis should be determined by the State or EPA depending on local conditions, and significant deviations from the "normal" range must be reported to the State or EPA and corrective actions taken immediately. The proposed regulations also limit the use of chlorine dioxide as a primary disinfectant to not exceed 1 mg/l because of possible adverse effects of by-products and would not permit the use of chloramines as primary disinfectants but only for maintenance of a distribution system residual.

EPA has also proposed that water systems subject to significant raw water contamination from pollution-related synthetic organic chemicals initiate a program to study, design and construct facilities utilizing granular activated carbon or equivalent technology to minimize human exposure to those contaminants.

In conclusion, I think the United States has come a long way in providing safe drinking water to her population. The Interim Primary Regulations and the proposed trihalomethane regulations are an important beginning. Our Revised Regulations, presently under consideration, will supplement our present efforts and begin to deal with contaminants where long-term impacts are beginning to be understood (especially carcinogens). However, in the future I see our attention being focused on the establishment of regulations that require specific water treatment for supplies that are shown to be at risk from specific contaminants. These regulations could specify disinfection, maximum contaminant levels for individual contaminants, coagulation and filtration, or other treatments when warranted. Such an approach is not only cost-effective, but in reality a sensible way to provide the public health protection needed.

I want to thank you for the opportunity to speak with you today and I look forward to working with you in the future as we together, in cooperation, provide safe drinking water to the citizens of our respective countries.

Y. Kott (Israel)

The surplus of water in the northern area of the country and severe scarcity in the south, the utilization of over 95 percent of the water potential in the country and the utilization of about 85 percent of the water for agricultural purposes, caused an intervention of the government to pass a law which nationalized all water resources from individual property to the public.

This law enabled the national water company to pump winter surplus water from lake Kinnereth and recharge it into sandy aquifer in the coastal plane through a dual-purpose well. During storage, water quality changed and the number of coliform bacteria rose up to 10^5/100 ml; turbidity was very high. Water quality improved at a long storage or due to continuous pumping. The various quality problems that have arisen by these operations caused the Ministry of Health to request a committee that was working on a new law for water quality to establish a quality criterion for such water. Indeed, the Israel Drinking Water Standard published in 1974 states at clause 14 that when drinking water is pumped from a dual-purpose well it should be examined and found to be free of fecal coliforms, streptococci and salmonella bacteria. In addition no more than two coliforms in 100 ml would be allowed and the water must be disinfected. As much as we know, no other country has as yet established this criterion in its water standard.

As already mentioned above, most of the water is used for agricultural purposes. The need for water has created a situation in which the farmers are ready to utilize various qualities of wastewater. It is estimated that reuse of wastewater will reach in the near future to over 120 million cubic meters. The importance of quality versus type of crop growth has brought to create new criteria for purified wastewater quality.

The irrigation with treated wastewater will have four quality levels in which the unlimited one will have to be 80 percentile of coliform, equal or less than 12, fecal coliform, fifty percentile 2.2/100 ml. Residual chlorine of 0.5 mg/l. It is mandatory that the water will have to pass sand filtration. On the other hand, group A which will allow irrigation of industrial crop like cotton, dry fodder, seeds etc. will allow BOD of 60 mg/l, suspended solids up to 50 mg/l.

The mechanism of utilizing most of the water resources and dividing the quality for each type of crop will maintain the true balance between needs and capability. It is thought that combination of utilization of all water resources for the various needs will postpone the need for water desalination from big plants which are much more expensive.

G. Müller (F.R.G.)

In Germany the addition of chlorine to drinking water is regulated by two laws, i.e. the Foodstuffs and Necessities Law and the Federal Epidemics Law. On the basis of these two laws statutory decrees have been laid down, one of these being a decree concerning the treatment of drinking water specifying the maximum amount of chlorine that can be added to drinking water. The amount in question is 0.3 mg Cl_2/l In times of emergency or disaster this value can be increased to 0.6 mg Cl_2/l. On the other hand, the Drinking Water Decree on the authorization of the Federal Epidemics Law lays down the minimum amount of chlorine when this is to be used as a disinfectant in drinking water. The chlorine content in drinking water leaving the works must be 0.1 mg Cl_2/l. In combination with this, chlorinated water ex works must not exceed a standard colony count value of 20 ml. The purpose of this combination is to guarantee the actual effectiveness of the chlorination.

The minimum and maximum values prescribed in the decrees for chlorine in drinking water show that in the Federal Republic the chlorine level permitted by law lies within very narrow limits.

Experience to date has shown that this chlorine content may be just sufficient to destroy pathogens entering the drinking water network by penetration of waste water or river water, especially since the organic substance flowing in at the same time consumes a large proportion of the chlorine before the disinfection occurs. This has been demonstrated time and again in recent decades in cases of typhoid and paratyphoid-B epidemics or epidemics due to other Salmonella species. The so-called safety chlorination normally makes it possible to reduce elevated colony counts, but is rarely sufficient for a reliable destruction of the pathogens that penetrate the supply network via short circuits, cross connections, and sucking back.

In Germany there are many public water supplies working on ground water that cannot be faulted from a bacteriological point of view, where the water is not chlorinated on leaving the works because bacterial proliferation, detectable by elevated colony counts, is simply not observed during the distribution or storage of the water.

J.A. Myhrstad (Norway)

The drinking water regulations in Norway are based on the Health Act, which is administered by the Ministry of Social Affairs.
According to the regulations, potable water should be hygienic, safe, the water source should be protected from microbiological and chemical pollution, and the water treated in a proper way.

The regulations also state that waterworks supplying between 100 and 1000 persons are subject to approval by the local Boards of Health, and the greater works are subject to approval by the National Institute of Public Health. Since there is no detailed information on how to proceed in order to achieve a wholesome potable water, it is the responsibility of these authorities to consider the necessary actions to be taken.

The waterworks can be given the right to expropriate land in the catchment areas and put restrictions on the existing and future activities, according to the Water Resources Act, in order to protect the water sources from pollution.

The Water Pollution Act is an important law which covers all forms of water pollution, and it contains a general prohibition, unless permission is granted, against most activities liable to cause water pollution. This law is administered by the Ministry of Environment.

According to the drinking water regulations, the waterworks are responsible for the water quality control. This control is very often carried out in close cooperation with the local Board of Health and National Institute of Public Health.

In addition to the analysis of raw water, treated water and tap water samples, plant control and weekly reports concerning communicable diseases in each community are integrated in the control procedure.

Surface water is by far the most important water source in Norway, at least for waterworks supplying more than 100 persons. About 95 % of the population supplied by these waterworks use surface water. The most important quality problems are related to the low pH-values of the surface water (down to a pH-value of 3.4), the very soft water (total hardness usually below 5-10 mg CaO/l) and the coloured water (e.g. colours in the range of 30-60 mg Pt/l).

Treatment problems are mainly related to low water temperatures in the winter time, which influence the coagulation process, and the coloured water being extensively used without adequate treatment, interfering with the chlorination process.

Chlorine is still the most important disinfectant used, but breakpoint chlorination is never achieved owing to the very small concentrations of ammonia (usually well below 0.1 ppm ammonia - nitrogen). There is a tendency to replace chlorine by ultraviolet irradiation. Chlorine dioxide will not be used until the health effect has been evaluated.
Examinations carried out have revealed high concentrations of trihalomethanes caused by chlorination of coloured water.

Other problems are related to the fact that many waterworks do not treat the water in the proper way, and that waterworks equipment, usually imported from abroad, is produced in countries with water qualities differing very much from the Norwegian water quality. One example is the asbestos-cement pipes without internal coating. Ca is extracted from the pipe material resulting in pH-values as high as 11.5. These pH-values increase the dissolution of heavy metals from taps made of brass alloys and solders. The asbestos-fibre content in the water will also be influenced.

We have no specific or detailed regulations concerning water quality, but we have recommendations. Some organic micro-pollutants are included in the recommendations; however, trihalomethanes are not included for the time being.

The present drinking water regulations will be revised in the near future.

An expert group has recently been appointed by the Royal Norwegian Council for Scientific and Industrial Research to evaluate the need for research in the field of drinking water supply.

G.J. Piet (The Netherlands)

In the Netherlands raw water sources for the drinking water supply consist of groundwater (650 million m^3/year) and surface water of the rivers Rhine and Meuse (400 million m^3/year).
In the treatment systems which are used for the drinking water supply chlorine is mainly used for disinfection, keeping the growth of bacteria in the distribution network under control, maintaining the quality of raw and pretreated water during transport, preventing strong bacterial growth on the walls of pipelines for raw and pretreated water, removing ammonium and incidentally converting ferrous salts into ferric salts. Disinfection should meet the highest requirements particularly where water may contain germs.

Though several groundwater stations and stations using bankfiltered water do not have to use safety-chlorination, chlorine must continue to be used as a disinfectant for potable water from a public health viewpoint. Restriction of the amount of chlorine dosed is proposed by carrying out disinfection as one of the last stages in the treatment when the water will be low in chlorine-consuming compounds.
Treatment systems such as dry-filtration to remove ammonia to avoid break-point chlorination and transport-purification instead of transport-chlorination are preferred to chemical oxidation procedures. Alternative chemical oxydants such as ozone and chlorine-dioxyde are studied to evaluate the effect on water quality. Not only chemical analyses of a wide variety of organic compounds formed under practical conditions in the waterworks are made and studied in more detail, but the results of mutageni-

city screening tests are already studied at this moment and will be a subject of thorough research in the near future.

On safety ground it is recommended that water should generally be treated by physical and biological processes to the greatest possible extent and that chemical oxidants should not be used more often than strictly necessary. However, the use of chlorine as a disinfectant will be replaced by other means only after their effects have been thoroughly studied and have proved to be fully acceptable.

An important subject which will be studied is the question of whether the risks of chemical oxydation are great enough to outweigh large claims on surface areas which are used at this moment, e.g. in dune infiltration. A deeper insight is necessary to evaluate the long-term risks to human health. Epidemiological studies are carried out at this moment for this purpose.

From the viewpoint of risks to human health standards or criteria for organic compounds in tapwater or raw water destined for the drinking water supply can only be set as interim regulations until more insight is obtained. Other aspects which are considered are future structural plans to obtain a reliable quality of potable water. The protection of raw water sources can be performed by water sanitation programs and protection of the underground against industrial pollution. Storage of pretreated water should be in places where aging of the water can occur, with avoiding further pollution.
Criteria for organics in drinking water will possibly be proposed not only for individual compounds but also for group- and sum parameters and possibly by a series of mutagenicity screening tests.

T. Stenström (Sweden)

Public water supplies in Sweden should, according to the law, be investigated bacteriologically with a frequency of at least once a week for large water supplies to once every third month for ground water supplies serving less than 4000 people. Private water supplies, usually hotels etc., should be checked in the same way. The chemical quality of the water is tested once a year. The samples are taken at the water-works.

Water is classified as not suitable if the total number of coliforms (MPN-method, 35°C, 48 h) is more than 10/100 ml. If this number is 1-9 or if the total plate count (22°C, 48 h) is more than 100 the water is classified as less suitable. The total plate count at 22°C is a valuable indicator of general contamination and of the efficiency of the water treatment and disinfection.

Private wells are also tested for fecal coliforms (MPN 44°C, 48 h). Such water is classified as unsuitable if the number of fecal coliforms is more than 10 or if the total number of coliforms is more than 500.

The chemical quality control is relatively similar to that recommended by WHO. Heavy metals and organic micropollutants are not analysed routinely. The only parameter used routinely for organic substances is permanganate consumption. A large survey for trihalometanes has, however, shown that most water supplies have concentrations below 10 µg/l of the trihalomethanes at the consumer's tap.

In only two cases out of 144 the concentration was above 100 µg/l.

The Swedish regulations from 1967 and 1970 should be revised in a few years. Recommendations for chemical and bacteriological monitoring of the water quality in distribution systems and at the consumer's tap will be published early in 1979. The purpose of this is

1) to extend the monitoring of parameters of importance for possible health effects to the consumer's tap, and
2) to provide data for making operational decisions in order to avoid problems like taste, odor or colour caused by corrosion or bacteriological activity in the network. For the bacteriological monitoring the membrane method will probably be accepted. It is not so today.

Of the water from public water supplies in Sweden 53% is surface water. 21% is infiltrated water usually from sandy ridges deposited during the glacial period. 26% is ground water without infiltration. About 15% of the population is not connected to public water supplies. They generally use ground water. Restrictions on the use of polluted surface waters as water supplies are not considered necessary in Sweden.

80% of the surface water is treated with chemical flocculation and filtration. Half of this water is also treated by slow sand filtration, for example by the water-works in Stockholm. Only rapid or slow sand filtration is used for 6 and 9% of the water, respectively.

The most common disinfectant is chlorine although chlorine dioxide is used in some water-works such as Gothenburg. Breakpoint chlorination as an oxidation step is not used. With very few exceptions the ammonia concentrations are below 0.5 mg/l and do not cause any problems except that nitrite up to a few tenth of a mg/l may be produced in the distribution system. Many water-works, e.g. Stockholm, add ammonia to get chloramines. Ozon is used only at two water-works.

Much of the Swedish research on drinking water problems is now focused on the deterioration of water quality during distribution. New treatment methods such as activated carbon filtration will also be studied. The philosophy is that water at the consumer's tap should be not only wholesome but of a high quality with regard to taste, odor and appearance.

Another problem, which should be studied, is the treatment at small water-works of water containing e.g. high concentrations of iron and manganese.

Except for some local areas, Sweden has no shortage of raw waters of a high quality. This is to a large extent due to strict regulations on the discharge of domestic and industrial sewage water. About 70% of the Swedish population living in cities and villages with more than 200 persons are now connected to waste-water-works with biological as well as chemical treatment. Another 26% has mechanical and biological treatment (usually active sludge). Only 3% has only mechanical treatment which is not accepted according to the law. An increasing number of waste-water-works is also supplied with a final filtration.

P. Toft (Canada)

Canada has a federal system of government and consists of 10 provinces and two territories. The distribution of powers between the provinces and the federal government is stated in the British North America Act of 1867. Although this Act does not deal specifically with water resources, and therefore drinking water supply, judicial interpretation over the years has resulted in a situation where there is a shared federal-provincial responsibility.

Under the Act, the ownership of natural resources, including water, is vested in the provinces. Thus the provinces have the primary authority to legislate in the area of municipal water supply.

Under their respective Health Acts the provincial departments of health also have the power to control conditions which constitute a threat to human health.

At the federal level, responsibility is assigned to the Department of National Health and Welfare to investigate and conduct programmes related to public health. For example, research and investigation into the health aspects of drinking water are undertaken with a view to public health protection. In carrying out such activities the Department is required to co-ordinate its efforts with those of the appropriate provincial authorities.

In Canada, drinking water is defined as a food and therefore in theory it could be regulated under the Food and Drugs Act. Although this has been done for bottled (mineral and spring) waters, standards have not been extended to tap water owing to the major role traditionally assumed by the provinces.

Generally the provinces play the lead role in ensuring an adequate and safe supply of drinking water whereas the Federal government provides leadership in ensuring adequate standards for drinking water quality especially to protect human health.

There are a few specific cases where the Federal government is solely responsible for drinking water. These include administering potable water regulations for all common carriers (transportation crossing Canadian Interprovincial and International borders), and on Canadian coastal shipping vessels, and the provision of potable water in the Territories, Indian reservations and military bases.

Standards

With the exception of a few provinces which specify that municipal water supplies must contain a certain minimal level of chlorine, there are no legally enforceable standards for drinking water supplies in Canada. Rather, there are guidelines for potable water quality and strict control over the design and operation of treatment plants. The federal government plays a lead role in establishing drinking water guidelines.

Revision of the Canadian Drinking Water Guidelines

It was in 1968 that the first Canadian Drinking Water Document was brought out by a joint committee comprising the Canadian Public Health Association Drinking Water Standards Committee and a federally-convened Advisory Committee on Public Health Engineering. The latter included representatives of the Federal and Provincial Departments of Health, several universities and Canadian water pollution and water resource control agencies. Provincial governments, in turn, have adapted these "guidelines" to suit their own particular situation. A joint federal-provincial group led by the Department of National Health and Welfare is currently revising the drinking water standards published in 1968.

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